HIGH TEMPERATURE THERMAL EXPANSIVITY AND SPECIFIC HEAT STUDIES OF SOME FACE CENTRED CUBIC METALS

A Thesis

presented by

Robert Campbell Pearson

to the

University of St. Andrews

in application for the Degree

of Master of Science

DECLARATION

I hereby declare that this thesis has been composed by me, is a record of work done by me, and has not previously been presented for a Higher Degree.

The work was carried out in the research laboratories of the Physics Department, St. Salvator's College, University of St. Andrews, under the supervision of Dr. J.L. Lawrence.

Robert Campbell Pearson.

CAREER

I obtained a National Diploma in Agricultural Engineering at the West of Scotland Agricultural College in 1959. After a few years in industry in Africa, I was appointed a lecturer at Elmwood Technical College and, in 1971, was promoted to Head of the Department of Engineering at that College.

CERTIFICATE

I certify that Robert Campbell Pearson has spent seven terms at research work in the Physical Science Laboratory of St. Salvator's College, in the University of St. Andrews, under my direction, that he has fulfilled the conditions of Ordinance No. 51 (St. Andrews) and that he is qualified to submit the accompanying thesis in application for the Degree of Master of Science.

Research Supervisor.

Acknowledgements

The author's thanks are due to Dr. J.L. Lawrence for guidance, advice and discussion. He also wishes to thank Dr. R.C.G. Killean for his encouragement to embark on the work, Professor J.F. Allen for the use of research facilities and Drs. Grant and Lisher for their interest and help. He is also indebted to Fife Education Committee who granted permission for him to be released from work on a regular basis to attend the University.

Abstract

Three methods of measuring the thermal expansivity of solids are reviewed, namely x-ray, interferometric and dilatometric methods and a description of the design, construction and operation of a dilatometer capable of measuring the thermal expansivity of solids from room temperature to about 1000K is given.

The effects of Schottky defects on thermal expansivity measurements are discussed and a method of measuring the concentration of these defects together with their energies and entropies of formation is given.

The thermal expansivities of lead, copper and aluminium, from room temperature to near the melting point of these elements, were measured. It was found that the thermal expansivities, α, for lead and copper varied linearly with temperature as

$$\text{Pb } \alpha = (21.14 \pm 0.21) \times 10^{-6} + (25.7 \pm 0.4) \times 10^{-9} T \text{ K}^{-1}$$

$$\text{Cu } \alpha = (14.07 \pm 0.09) \times 10^{-6} + (6.98 \pm 0.15) \times 10^{-9} \text{ K}^{-1}$$

Aluminium, however, was found to vary non-linearly with temperature and above 750K the values for α for a fall in temperature were significantly greater than those for a rise in temperature and an explanation of this phenomenon is given. In all three cases close agreement exists between the present expansivity results and those of other workers.

Comparison between the theoretical specific heat as obtained from the Debye model and experimental values is made. The experimental values of specific heat at constant pressure were corrected for dilation, electronic and energy effects, these corrections and their effects being explained and detailed. Any discrepancy found to

arise between the Debye specific heat and the specific heat determined from experiment is referred to as "excess specific heat", ΔC_v. The analysis was performed on five face centred cubic metals from room temperature to the melting point of the elements and approximate linear relationship between ΔC_v and temperature was established for lead. For aluminium and gold, different results for different sets of experimental data were obtained and no excess specific heat was detected for copper and silver. Considerable discrepancies are reported between different sets of published specific heat values and it was concluded that further progress in the verification of the theory of solids using high temperature specific heat data can only be achieved when more consistent results are available.

Finally, the Grüneisen "constant" and its temperature dependence for these five metals was investigated. The Grüneisen "constant", G, was found to increase with temperature for all these materials, the increase being fairly linear for lead, aluminium, gold and copper according to the expressions

Lead $\quad G = (2.59 \pm 0.03) + (6.7 \pm 0.6) \times 10^{-4} T$

Aluminium $\quad G = (2.03 \pm 0.05) + (5.5 \pm 0.8) \times 10^{-4} T$

Gold $\quad G = (2.97 \pm 0.04) + (3.8 \pm 0.4) \times 10^{-4} T$

Copper $\quad G = (1.92 \pm 0.02) + (2.0 \pm 0.2) \times 10^{-4} T$

For silver, G varied little with temperature and an approximate relationship may be

Silver $\quad G = (2.42 \pm 0.02) + (0.6 \pm 0.3) \times 10^{-4} T$

In all cases close agreement existed between previous literature G values and the present results.

Contents

CHAPTER 1

INTRODUCTION

The work described in this thesis deals with the measurement of thermal expansivities of some face centred cubic metals along with an analysis of previously published high temperature specific heat data.

In the solid state the mean positions of atoms are fixed in space and the environment of a particular atom is exactly the same as that of many other atoms in the solid. Hence any theory describing the behaviour of such atoms must be essentially different from theories describing liquids and gases where the atoms are free to alter their position relative to each other in space. Owing to the nearness of neighbouring atoms, each atom cannot be considered as being independent of its neighbours and its motion will depend on the magnitude of the interatomic forces. Any theory which successfully describes the thermodynamic properties of real solids must be able to predict these interatomic forces, from which the distribution of frequencies and energies of the vibrating atoms may be obtained. Of these properties, this thesis is particularly concerned with the temperature dependence of thermal expansivity and specific heat.

Many successful theories in solid state physics are based on a "harmonic approximation" which assumes that the force on a vibrating atom is proportional to its displacement from the mean position and therefore the motion of the atoms is of a simple harmonic nature. This approximation is valid provided the displacements are small and the potential energy, $V(x)$, of an atom at a distance x

from its mean position can be written in the form

$$V(x) = V_o + \tfrac{1}{2}Kx^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1.1)$$

where K is a constant.

However many well known physical effects cannot be accounted for on the basis of the "harmonic approximation" and these are known as "anharmonic effects". Some common examples of anharmonic effects are the variation of elastic constants with temperature, the departure from linearity of the temperature dependence of the Debye-Waller factors and the presence of thermal expansion. The latter is one of the easiest effects to observe and measure and it forms the basis of the discussion in Chapter 2.

Thermal expansivity can be understood by assuming that the pair potential between two atoms lacks mirror symmetry and cannot be expressed in the form of equation (1.1). Figure 1 shows the potential energy of a pair of atoms as a function of their separation. At absolute zero the equilibrium position (ignoring zero point energy) is at Z, so the equilibrium separation is YZ. As the temperature is raised and the atom vibrates between P and Q, the mean separation of the atoms will have moved to Y'Z' which, because of the asymmetry in the shape of the potential curve, is greater than YZ. Thus the mean separation increases with temperature along the curve Z, Z', Z", shown as a locus of points in figure 1, and a consequent increase in the dimension of the solid will occur. Although this theory tends to simplify the problem, it does give an insight into the mechanism of interatomic expansions. In a purely harmonic lattice the potential energy curve is symmetric about the line ZR and as a result there would be no lattice expansion because

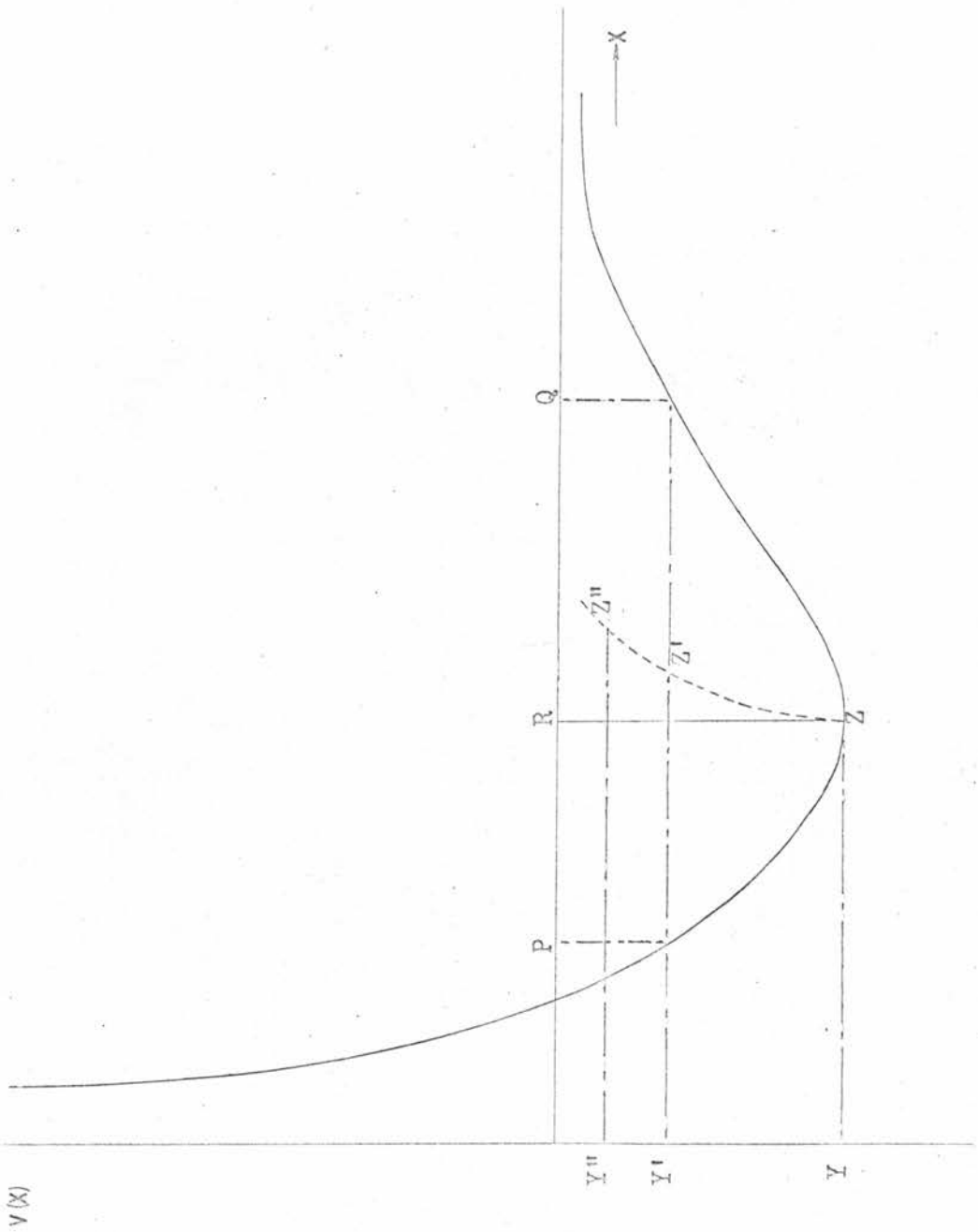


Figure 1 Potential energy V(X) for a pair of atoms, separation X.

the interatomic separation would be always YZ for all energies.

In Chapter 2 the various methods of measuring thermal expansivities are reviewed and the design construction and use of apparatus, based on one of these methods, the high temperature dilatometer, is described.

Chapter 3 deals with the analysis of high temperature specific heat data. In this thesis the term specific heat refers to the molar specific heat, C, which is defined as the quantity of heat required to raise the temperature of 1 gram mole of the material by 1K, and is given by

$$C = \frac{dU}{dT}$$

where dU is the quantity of heat required to raise the temperature of 1 gram mole by dT.

Specific heat varies with temperature and several theoretical models have been proposed to explain this effect. One of the most successful of these is due to Debye (1912). In this model the atoms are considered to be a system of coupled harmonic oscillators and the predicted specific heat is zero at OK and rises to a constant value at high temperatures. Although the observed temperature dependence follows this predicted behaviour fairly closely, discrepancies have been found to arise at high temperatures where the harmonic approximation is no longer valid and higher order terms in the pair potential give significant contributions to the specific heat. In the present work these discrepancies have been investigated by comparing the values of the specific heat obtained from the Debye model with experimental values which have been corrected for dilation, electronic and vacancy energy effects, and any differences are called

"excess specific heat". The analysis was performed for five face centred cubic metals namely lead, aluminium, copper, gold and silver and the temperature dependence of the Grüneisen "constant" for these materials was investigated.

CHAPTER 2

EXPERIMENTAL DETERMINATION OF THERMAL EXPANSIVITIES

1. Experimental Methods

Any method of accurately determining the thermal expansivities of solids must achieve the precise measurements of very small displacements. For example, the length of a bar of copper, 1 cm long, increases by 17×10^{-6} cm for a 1K rise in temperature at room temperature. This chapter discusses both x-ray and interferometric techniques for measuring expansivities and describes the construction and operation of a high temperature dilatometer to measure the thermal expansivity of solids over a wide temperature range.

X-ray Diffraction Technique

When a monochromatic beam of x-rays is diffracted by a crystalline material, the positions of the diffraction maxima are functions of the direction of the incident beam and the size of the unit cell of the crystal. If the temperature of the sample is increased, resulting in an expansion of the material and an increase in the size of its unit cell, the positions of the diffraction maxima will change. A measurement of this change will enable the thermal expansivity of the material to be found.

The position of the maxima is determined by Bragg's Law

$$2d \sin \theta = n\lambda \qquad .. \quad .. \quad .. \quad (2.1)$$

where d is the separation of the diffracting planes,

θ is the Bragg angle,

n is an integer

and λ is the wavelength of the x-rays.

The angular change in the position of a diffraction maxima, $\Delta\theta$, can be derived by the differentiation of equation (2.1) and is

$$\Delta\theta = -\left(\frac{\Delta d}{d}\right)\tan\theta \qquad (2.2)$$

where Δd is the increase in the separation of the diffracting planes. Obviously, for large values of $\Delta\theta$, Bragg angles as close as possible to 90° should be used and hence a long wavelength radiation is desirable. The angular change, $\Delta\theta$, in the position of the diffraction peaks is determined by measuring the movement of these peaks round the circumference of an x-ray camera, the radius of which should therefore be made as large as possible. Such a camera was designed by Wilson (1941) and was used to determine the thermal expansivity of aluminium. The camera had a radius of about 10 cm and, therefore, for a temperature rise of 100K and a Bragg angle of about 45°, the movement in the position of the maxima on the x-ray film was approximately 0.03 cm.

The main advantage of the x-ray technique is that it involves the measurement of the change in lattice parameter and not in the overall dimension of the sample and, thus, the results are not complicated by the problems of sublimation or vacancy formation associated with macroscopic techniques. It also has the advantage that small, irregularly shaped samples of unknown dimensions can be used.

The disadvantages are (1) the complications involved in building an x-ray camera in conjunction with a furnace, (2) the increase in the general background intensity that occurs as the temperature increases, making the estimate of the position of the diffraction peaks uncertain, and (3) the restriction that the method

can only be used for crystalline powders or single crystals.

Interferometric Technique

The interferometric method of Fizeau permits the measurement of the thermal expansivity of samples of relatively large dimensions. The sample is placed between two parallel semi-reflecting surfaces through which passes a monochromatic beam of light. Interference fringes are formed due to a phase difference between light reflected from the two surfaces, and, if they move relative to each other, the phase difference alters and the fringes appear to move. This movement enables an accurate measurement to be made of the displacement between these two surfaces.

Many researchers have developed this technique, the most recent being Hahn (1970) in his work to establish copper as a standard reference material. In his interferometer, three 1 cm specimens of copper were clamped at equal intervals around a copper ring specimen holder to which was attached a Pt versus Pt-10% Rb thermocouple. This ring was placed between two fused quartz interferometer plates and adjusted to provide optimum fringe separations when illuminated by a mercury source, the whole system being evacuated. This type of equipment provided a high degree of accuracy with the error in each measurement of expansivity being $\pm$ 0.05 x $10^{-6}K^{-1}$. However, errors may be larger than this if the experiment is carried out in air because of the presence of air films and the formation of oxide layers.

High Temperature Dilatometric Technique

The x-ray diffraction technique can be used to measure the fractional increase in the size of a unit cell, $\Delta a/a$, which occurs

during expansion. However, when a dilatometer is used with a bulk sample, a measure of the fractional change in the overall length of the solid, $\Delta\ell/\ell$, is obtained. In the past, these measurements were made using micrometers, microscopes and dial gauges. Recently it has been the practice to use linear differential transducers, which transfer the mechanical movement of a sample into electrical variations, making it possible to measure very precise changes in length. Such a system, incorporating a furnace, an extension rod and a transducer has been designed, and details of its construction and usage are given later in this chapter.

2. Lattice Defects and their Effect on Thermal Expansivity

The orderly nature of the arrangement of atoms in crystalline materials can be disturbed by defects which have a marked effect on some physical properties of these substances. In particular there are two main types of defect which can affect the apparent thermal expansivity. The first type of defect involves the removal of atoms from atomic sites and is known as "vacancy formation" whereas the second type involves the introduction of extra atoms into non-regular atomic sites and is called "interstitial formation".

A particular kind of vacancy, known as a Schottky defect, occurs when an atom gains sufficient thermal energy to move out of its lattice position and migrate to the surface of the crystal. This will result in an increase in the size of the sample but not in the size of the unit cell and thus the thermal expansivity of the material measured by the dilatometric technique will be greater

than that measured by the x-ray technique. The difference between the two expansivities can be used to provide information on the density of vacancies in solids and the corresponding energies required to produce them.

In any real crystal, at a temperature T, there exists an equilibrium atomic fraction of the jth type of defect given by (Damask and Dienes, 1963)

$$C_j = \frac{n_j}{N} = \exp\left(\frac{\Delta S_j}{k}\right) \exp\left(\frac{-W_j}{kT}\right) \quad .. \quad .. \quad .. \quad (2.3)$$

where n_j is the number of such defects,

N is total number of atoms present,

ΔS_j is the entropy of formation of the defect,

and W_j is the energy of formation of the defect.

The types of vacancies which can occur are monovacancies, divacancies and trivacancies where one, two or three neighbouring atoms respectively are missing from a region in a solid. Monovacancies are much more common in elements (Simmons and Balluffi, 1960) and it will be assumed that only monovacancy formation has any effect on the thermal expansivity.

If an increase in temperature dT produces an increase in the number of monovacancies, dn, this will result in an increase in the size of the specimen and give an apparent increase in the thermal expansivity of

$$\Delta\alpha = \frac{1}{3N}\frac{dn}{dT}$$

This apparent increase $\Delta\alpha$, due to monovacancy formation, can be equated to the difference between the expansivity measured by dilatometer to the expansivity measured by means of x-rays.

$$\therefore \Delta\alpha = \frac{1}{\ell}\frac{d\ell}{dT} - \frac{1}{a}\frac{da}{dT}$$

where ℓ is the length of the sample,

and a is the unit cell dimension.

Integrating the two expressions for $\Delta\alpha$ with respect to T gives

$$\int \Delta\alpha \, dT = \int \frac{dn}{3N} = \frac{n}{3N} = \frac{C}{3}$$

and

$$\int \Delta\alpha \, dT = \int \frac{d\ell}{\ell} - \int \frac{da}{a} = \left(\frac{\Delta\ell}{\ell} - \frac{\Delta a}{a}\right)$$

where $\Delta\ell$ and Δa are the total increases in the length of the specimen and unit cell dimension respectively.

$$\therefore C = 3\left(\frac{\Delta\ell}{\ell} - \frac{\Delta a}{a}\right)$$

From this equation, a measurement of the difference between $\Delta\ell/\ell$ and $\Delta a/a$ will give a measure of the vacancy concentration, C., and the energy of formation may be obtained from

$$\Delta\alpha = \frac{1}{3N}\frac{dn}{dT}$$

$$= \frac{1}{3}\exp\left(\frac{\Delta S}{k}\right)\frac{W}{kT^2}\exp\left(\frac{-W}{kT}\right)$$

$$= \frac{C}{3}\frac{W}{kT^2}$$

If the defects are interstitials, this would result in a decrease in the sample size and $\left(\frac{\Delta\ell}{\ell} - \frac{\Delta a}{a}\right)$ would be negative. For most materials, however, the possibility of the production of interstitials is much smaller than that for vacancies.

Simmons and Balluffi (1960a, 1960b) have used this relationship to determine experimentally the fractional density of vacancies in aluminium and in other materials by simultaneously measuring the

macroscopic and x-ray expansions. Their apparatus is shown in figure 2. The specimens, 50 cm long, were housed in a specially prepared graphite core. The graphite provided a smooth inert support allowing free expansion and contraction of the specimen and, by virtue of its high thermal conduction, protected the specimen against thermal gradients.

All temperatures were measured with a Pt versus Pt-10% Rh thermocouple which could be moved parallel to the specimen in order to ascertain the temperature at any point. The furnace, enveloping the sample, was of the resistance heating type, specially constructed to provide thermal equilibrium, with a system of ports to allow micrometer readings to be taken and x-rays to reach the samples. Specimens of high purity were used and the x-ray diffraction measurements were taken from a suitably orientated large grain near the centre of the bar. $\Delta l/l$ was measured by observing the movement of reference marks on the specimen surface with two parallel mounted micrometer microscopes. In a typical length measurement, the specimen along its whole length was maintained at constant temperature ($\pm$ 0.2K) and at least 10 consecutive pairs of microscope readings were taken over a period of 7 minutes and a measurement of the average temperature of the bar over this period was also determined.

Simultaneously x-ray lattice expansion measurements were made using $NiK\alpha_1$ radiation whose beam was oscillated over the crystal with an amplitude of 40' of arc. The diffracted beam was photographed on a film at a distance of 70 cm from the camera, for an exposure time of between 5 to 7 minutes with an average temperature at the crystal being found. $\Delta a/a$ was then obtained from equation

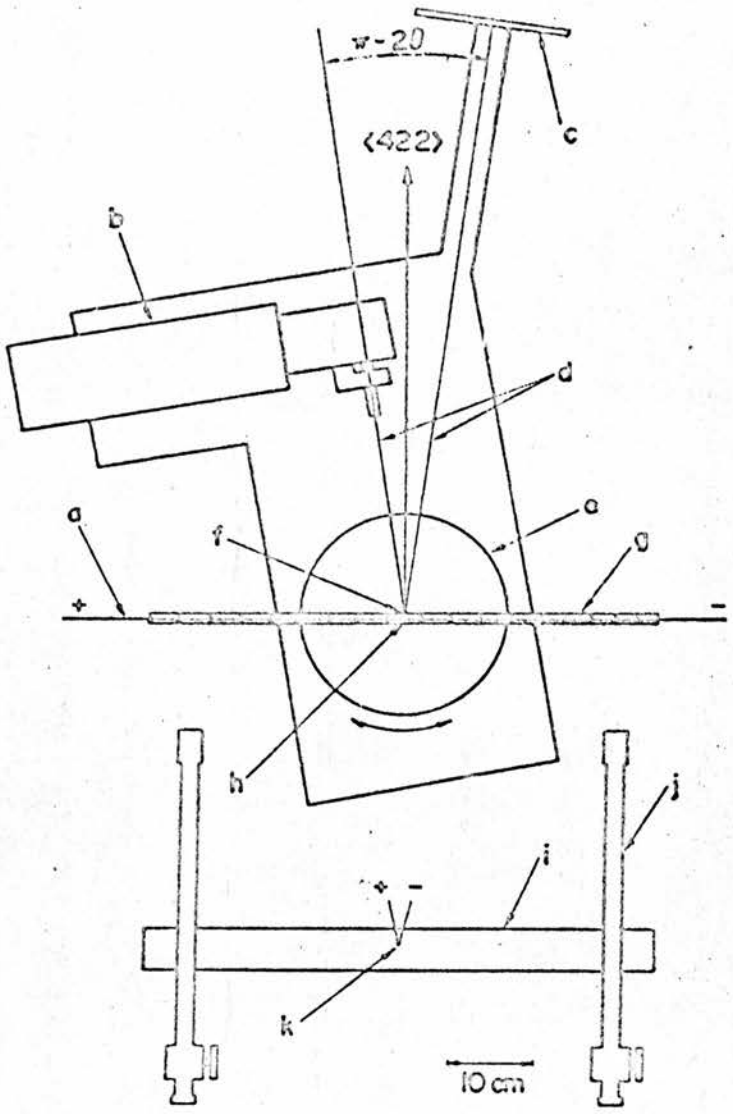


Figure 2 Schematic top view of apparatus used for length and x-ray lattice expansion measurement. *a* = butt-welded Pt *versus* Pt-10% Rh thermocouple, *b* = x-ray tube and collimator, *c* = film cassette, *d* = path of incident and diffracted x-rays, *e* = rotating stage supporting x-ray tube platform and film cassette arm, *f* = vertical axis of rotation of x-ray apparatus, *g* = specimen (polycrystal possessing "bamboo" structure), *h* = x-ray crystal, *i* = Invar mounting bar for microscope assembly, *j* = filar micrometer microscope equipped with relay lens, *k* = thermocouple.

(2.2) since, for a material with cubic crystalline symmetry, $\Delta a/a = \Delta d/d$.

Experimental Results

Simmons and Balluffi's values of $\Delta \ell/\ell$ and $\Delta a/a$ for aluminium are shown in figure 3 for the temperature range 229°C - 655°C with 20°C taken as the reference temperature for both heating and cooling curves. At about 500°C $\Delta \ell/\ell$ becomes noticeably greater than $\Delta a/a$ and this difference increases continuously up to melting point. The reversible nature of the high temperature divergence of the two curves confirms the reversible behaviour of the defect formation.

This net difference is due to all types of vacancies but Simmons and Balluffi have shown that, for aluminium, monovacancies are mainly responsible and they deduced the values of the entropy and energy of formation of these defects to be

$$\Delta S/k = 2.4 \pm 0.2; \quad W = (0.76 \pm 0.01)\ eV$$

The results of other work carried out by Simmons and Balluffi for monovacancy formation in other materials are shown in the table below.

	$\Delta S/k$	W(eV)
Silver (1960b)	1.5	(1.09 ± 0.09)
Copper (1963)	1.5	(1.0 ± 0.1)
Gold (1962)	0.5	(0.94 ± 0.09)

3. Design and Construction of High Temperature Dilatometer

The important factors which had to be taken into account in the design and construction of the dilatometer used in the present

work were the elimination of unwanted thermal expansion and mechanical hysteresis, the minimisation of friction between moving parts and the protection of the transducer from excessive heat. The apparatus is illustrated in figure 4.

The sample is placed on an anvil, at the base of a silica glass tube of diameter 2.5 cm, via an access port cut in the side of the tube. The sample is connected to the shaft of the transducer by means of a silica push rod, silica glass being used because of its low thermal expansivity ($0.5 \times 10^{-6} K^{-1}$) and high melting point. The silica tube is fixed between two firmly supported metal clamping plates on top of which is a stainless steel cylinder which houses the transducer, the overall length of the transducer and tube being 24 cm. The top of the cylinder is fitted with a threaded cap which, when screwed down, enables the iron core of the transducer to be placed near to the centre of the primary coil giving a very small voltage output. The whole apparatus is supported by three legs joined to the metal clamping plates. Further insulation is provided, at the neck of the furnace, by packing 4 cm of the silica tube with powdered magnesium oxide to prevent furnace heat loss and to provide protection for the transducer. Above 1100K, silica begins to transfer heat by radiation and this problem was overcome by internally staining 1 cm of the rod with a blue cobalt salt to absorb the heat energy.

Figure 5 shows a schematic diagram of a linear differential transducer. An iron core is located inside the windings of a primary coil at either end of which are situated two secondary coils whose outputs are connected in series opposition. As the position of the core is varied in relation to the secondary coils, the

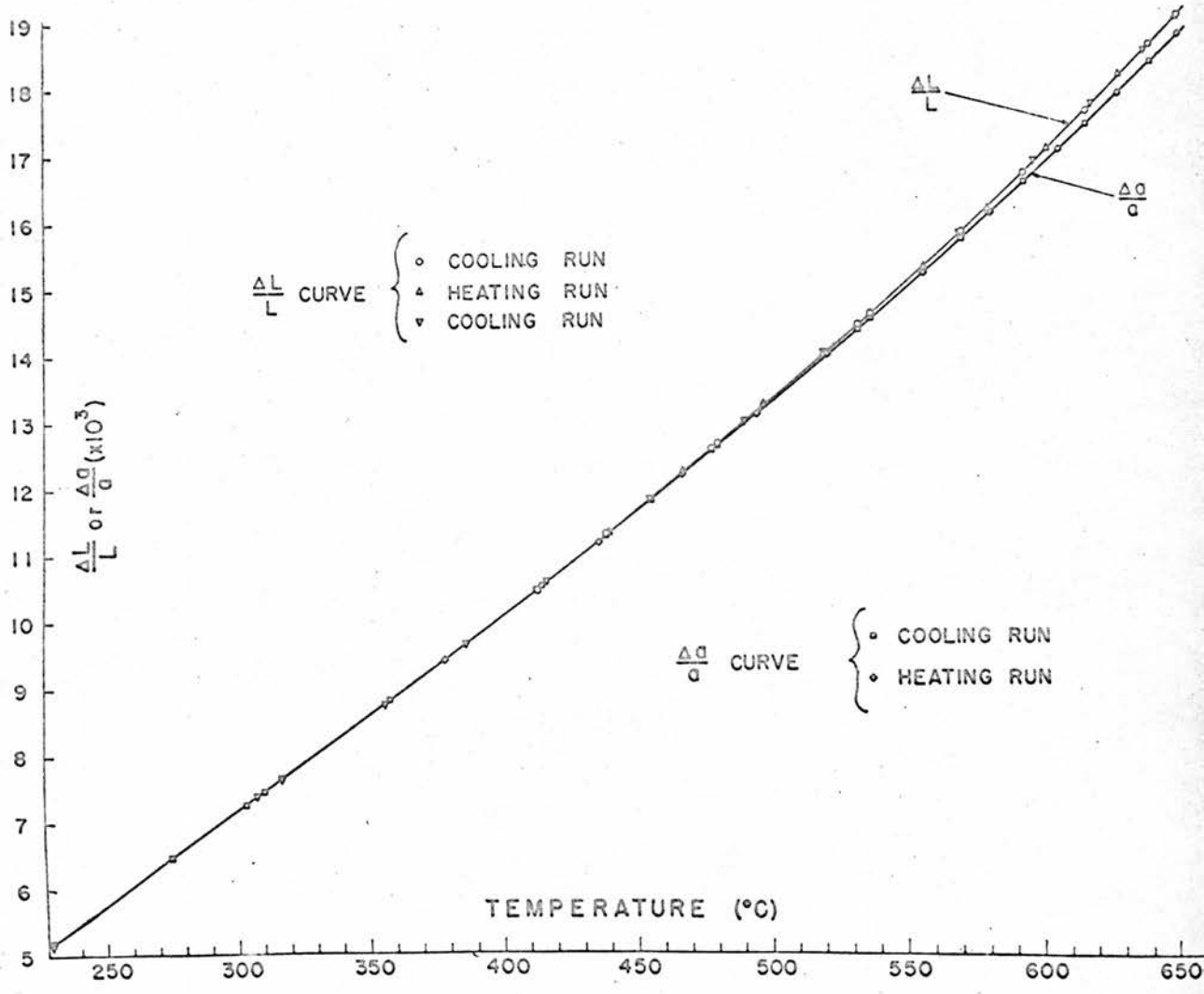


Figure 3 Simmons and Balluffi's measurements of the expansion of aluminium by x-ray ($\frac{\Delta a}{a}$) and macroscopic ($\frac{\Delta L}{L}$) methods.

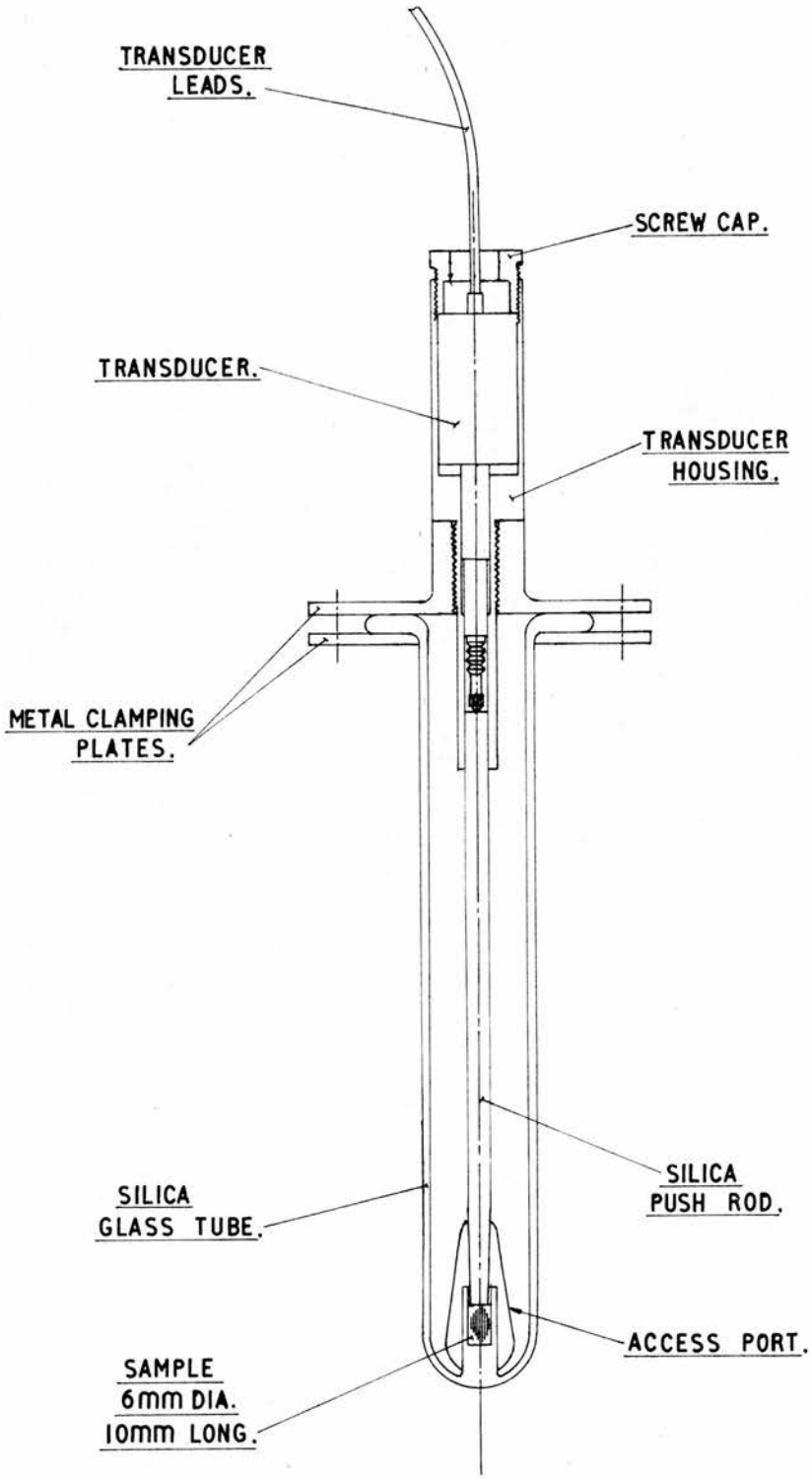


Figure 4 Cross-sectional diagram of the dilatometer and transducer with sample in place.

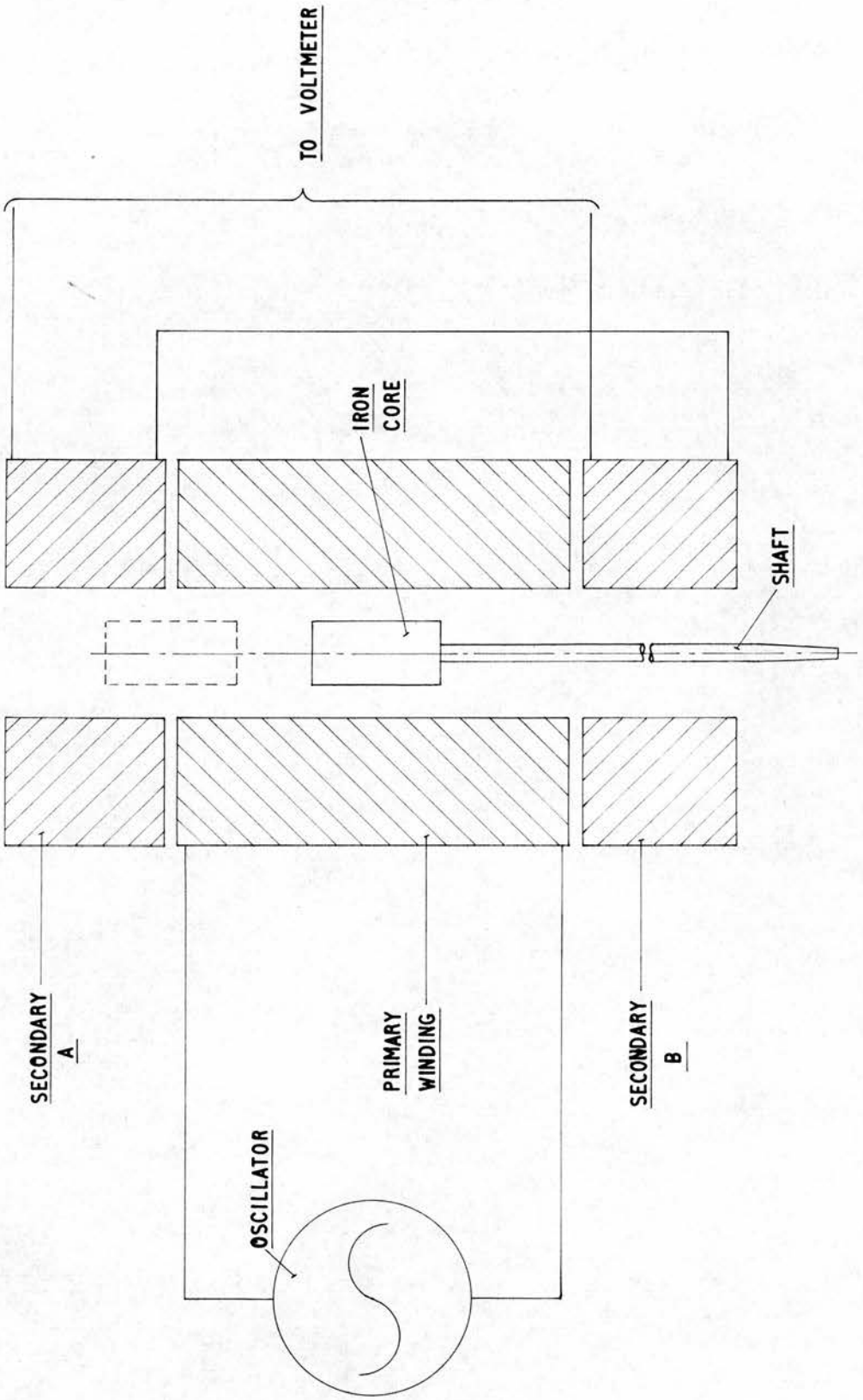


Figure 5 A schematic diagram of the linear differential transducer.

different voltage induced in each will result in a net output voltage. This voltage is proportional to the displacement of the core to which the sample is attached via the push rod and shaft. The transducer used was model ER/0.100 manufactured by Sangamo Western Control Limited, working on D.C. input and output. As well as the primary and secondary coils, the instrument comprised (1) a transistor oscillator, the output of which is fed to the primary winding, (2) a phase sensitive transistor detector circuit and (3) a passive filter network.

The input to the transducer was from a Farnell stabilised power supply Model E30/1 which could produce up to 30 volts with a stability of 0.039%. The output voltage was measured on a Keithly digital multimeter, Model 100, capable of reading $\pm$ 1μ V.

The electrical resistance furnace was constructed out of a 20 cm cube of low density firebrick encased in a 2 cm layer of glass wool with an outer shield of 2 cm thickness of polystyrene. The resistance heating element was 100 cm of Kanthal A of diameter 0.8 cm wound longitudinally round a cylindrical quartz former of height 3 cm and diameter 3.5 cm placed at the centre of the tube. An access port, slightly wider than the silica tube, was drilled from the top of the cube to the centre. The sample could thus be lowered into the furnace so that it was situated towards the base of the quartz former where the temperature gradients were minimal. A Ni-Cr/Ni-Al thermocouple was positioned within the heating chamber so that it was in close proximity to the sample and the temperatures were read from a Comark Digital Thermometer 3000.

4. Transducer Calibration and Experimental Technique

Since the expansivities were to be determined from measurements of the output voltage from the transducer, it was necessary to calibrate the instrument over the total range of output voltage which was expected to be about $\pm$ 200 mV. This was achieved by firmly clamping both the transducer and a depth micrometer to a suitable support, with the end of the transducer in contact with the spindle of the micrometer. The micrometer spindle was then extended until an output of $\pm$ 200 mV was obtained and then the whole arrangement was left for 30 minutes to stabilize. The spindle was then advanced in units of 5×10^{-3}cm and output readings taken at these intervals. Below is a table showing a typical set of results from one calibration run, and the least squares straight line fit gave a shift of (49.98 ± 0.10)mV for a movement of 5×10^{-3}cm. Two similar transducers were used in the experiments, the calibrations being frequently checked.

Voltage on Transducer = 15V

Micrometer Reading cm x 10^3	Voltmeter Reading in mV
15	+ 170.8
20	120.6
25	71.0
30	20.7
35	- 29.0
40	- 70.1
45	- 128.9
50	- 179.1

The calibration is usually expressed in units of $mVV^{-1}cm^{-1}$ and in this case, since the voltage to the transducer was 15.0V, the calibration factor Y was

$$Y = 49.98 \text{ mV per 15V per } 5 \times 10^{-3}\text{cm}$$
$$= (664 \pm 1)mVV^{-1}cm^{-1}$$

The thermal expansivity, α of a substance of length ℓ whose length increases by $d\ell$ when its temperature increases by dT, is given by

$$\alpha = \frac{1}{\ell}\frac{d\ell}{dT}$$

In practice α is determined experimentally by measuring the total change, $\Delta\ell$ resulting from a rise in temperature ΔT using

$$\alpha = \frac{1}{\ell}\frac{d\ell}{dT}$$

and the apparent thermal expansivity of the material is obtained from

$$\alpha = \frac{y}{\ell VYt_r}$$

where y = change in output voltage of transducer for a rise in temperature t_r(mV)

and V = transducer input voltage (V).

However, as the material expands, the silica glass also expands and the change in the length of the material measured is actually the difference between the real expansion of the material and the expansion of an equal length of silica whose thermal expansivity, $(0.5 \times 10^{-6})K^{-1}$, is very small and is almost independent of temperature. Thus the true thermal expansivity of the material is given by

$$\alpha = (\frac{y}{\ell VYt_r} + 0.5 \times 10^{-6})K^{-1} \quad .. \quad .. \quad .. \quad (2.4)$$

Due to unavoidable fluctuations in the transducer output of the order of $\pm$ 20 μV the output voltages were measured to $\pm$ 0.1 mV. In the results for lead to be described later, a change in temperature of 50K resulted in a change of output of $\pm$ 20 mV. The error in y was therefore 0.5%, while the error in t_r was about 2%. Obviously greater accuracy could have been achieved by using a larger temperature range but the equation 2.4 assumes α over the temperature range to be a constant and, since α is usually a function of temperature, small values of y and t_r must be taken.

It was therefore necessary to choose a temperature range sufficiently large to minimise the error in temperature measurement and yet small enough to be able to detect variations in thermal expansivities.

The furnace was placed on a vibration-free table. Each sample was in the form of a cylinder approximately 1 cm long and carefully ground to ensure that the flat surfaces were parallel. The length of the samples were measured accurately by a micrometer at room temperature. Each was then placed in turn on the silica anvil, and, with the push rod in position, the sample and lower part of the silica tube were lowered into the furnace with the apparatus firmly resting on its three supporting legs on the table. The power supplies and measuring instruments were switched on and allowed to stabilize for 30 minutes. At the end of this period the power input to the transducer was recorded and periodically checked for constancy during the experiment. The transducer was then placed in its holder and adjusted until its output was about $\pm$ 200 mV. The whole system was then given further time to stabilize and the first recording only commenced when all the instrument readings had remained steady for a reasonable time.

The temperature of the sample was raised (mode A) through temperature intervals of 50K and a constant temperature maintained for about 5 minutes to ensure both thermal equilibrium and accurate readings of transducer output. A similar procedure was used on cooling the sample (mode B). The thermal expansivities were then calculated for modes A and B at the mid-point of the temperature interval.

5. Thermal Expansivity Results for Lead, Copper and Aluminium

Lead

The experimental studies on lead were designed to produce information on the reproducibility of the apparatus and to yield detailed results on the variation of the thermal expansivity with temperature.

The expansivity was measured many times for both modes A and B in the temperature ranges 303K to 343K and 553K to 593K. The results listed in table 1 show that the values of α obtained at the lower temperature were reproducible giving an average value of $(29.3 \pm 0.1) \times 10^{-6} K^{-1}$ at 323K. A close study of the results at the higher temperature indicates that expansivities measured by mode A were slightly lower than those measured by mode B, the average expansivities being $(35.6 \pm 0.1) \times 10^{-6} K^{-1}$ and $(35.9 \pm 0.1) \times 10^{-6} K^{-1}$ respectively at 573K.

The thermal expansivity of lead from room temperature to its melting point (600K) was then measured using modes A and B. A set of experimental results are shown in table 2 and the average values obtained from five runs are listed in table 3 and shown graphically

Table 1

Lead - High and Low Temperature Runs

$V = 14.53V$

$Y = 770\ mVV^{-1}cm^{-1}$

$\ell = 1.010$ cm at 293K

$\alpha = (\frac{88.49V}{t_r} + 0.50 \times 10^{-6})K^{-1}$

T(K)	t_r	mV	y	$\alpha(\times 10^6)K^{-1}$	T(K)
303		103.4			
	40		13.0	29.3	323
343		90.4			
	40		13.1	29.5	323
303		103.5			
	40		13.0	29.3	323
343		90.5			
	40		13.0	29.3	323
303		103.5			
	40		13.0	29.3	323
343		90.5			
	40		13.0	29.3	323
303		103.5			
	40		13.0	29.3	323
343		90.5			
	40		13.0	29.3	323
303		103.5			

T(K)	t_r	mV	y	$\alpha(\times 10^6)K^{-1}$	T(K)
553		-63.2			
	40		15.9	35.7	573
593		-79.1			
	40		16.1	36.1	573
553		-63.0			
	40		15.9	35.7	573
593		-78.9			
	40		15.9	35.7	573
553		-63.0			
	40		15.8	35.3	573
593		-78.8			
	40		16.0	35.9	573
553		-62.8			
	40		15.9	35.7	573
593		-78.7			
	40		15.9	35.7	573
553		-62.7			

Table 2

Lead - Sample Results

$V = 14.53V$

$Y = 770\ mVV^{-1}cm^{-1}$

$\ell = 1.010$ cm at 293K

$\alpha = (\frac{88.49V}{t_r} + 0.50 \times 10^{-6})K^{-1}$

T(K)	t_r	mV	y	$\alpha(\times 10^6)K^{-1}$	T(K)
295	78	186.2	25.6	29.6	334
373	50	160.6	17.6	31.7	398
423	50	143.0	18.2	32.7	448
473	50	124.8	18.9	34.0	498
523	50	105.9	19.7	35.4	548
573	50	86.2	19.8	35.5	548
523	50	106.0	18.7	33.6	498
473	50	124.7	19.0	34.1	498
523	50	105.7	19.7	35.4	548
573	50	86.0	19.5	35.0	548
523	50	105.5	18.8	33.8	498
473	50	124.3	18.1	32.5	448
423	50	142.4	17.4	31.3	398
373	50	159.8	16.7	30.1	348
323	50	176.5	16.8	30.2	348
373	50	159.7	17.5	31.5	398
423	50	142.2	18.1	32.5	448
473	50	124.1	18.0	32.4	448
423	50	142.1	17.5	31.5	398
373	50	159.6	16.7	30.1	348
323		176.3			

Table 3

Lead - Values of Thermal Expansivities ($\times 10^6$)

T(K)	αK^{-1}	T(K)	αK^{-1}	T(K)	αK^{-1}
323	29.3 29.5 29.3 29.3 29.3 29.3 29.3 29.3 29.30	373	31.1 30.8 30.7 30.7 30.7 30.8 30.80	398	31.7 31.2 31.5 31.5 31.6 31.6 31.53
T(K)	αK^{-1}	T(K)	αK^{-1}	T(K)	αK^{-1}
423	31.9 31.8 32.0 32.0 32.0 31.9 31.93	448	32.7 32.5 32.5 32.4 32.7 32.4 32.53	473	33.0 33.6 33.7 33.4 33.2 33.2 33.35
T(K)	αK^{-1}	T(K)	αK^{-1}	T(K)	αK^{-1}
498	34.0 33.6 34.1 33.8 33.8 33.9 33.86	523	34.6 34.5 34.4 34.5 34.4 34.6 34.50	548	35.4 35.5 35.4 35.0 35.5 35.3 35.35

T(K)	Mode A	T(K)	Mode B
573	35.7 35.7 35.3 35.7 35.60	573	36.1 35.7 35.9 35.9 35.90

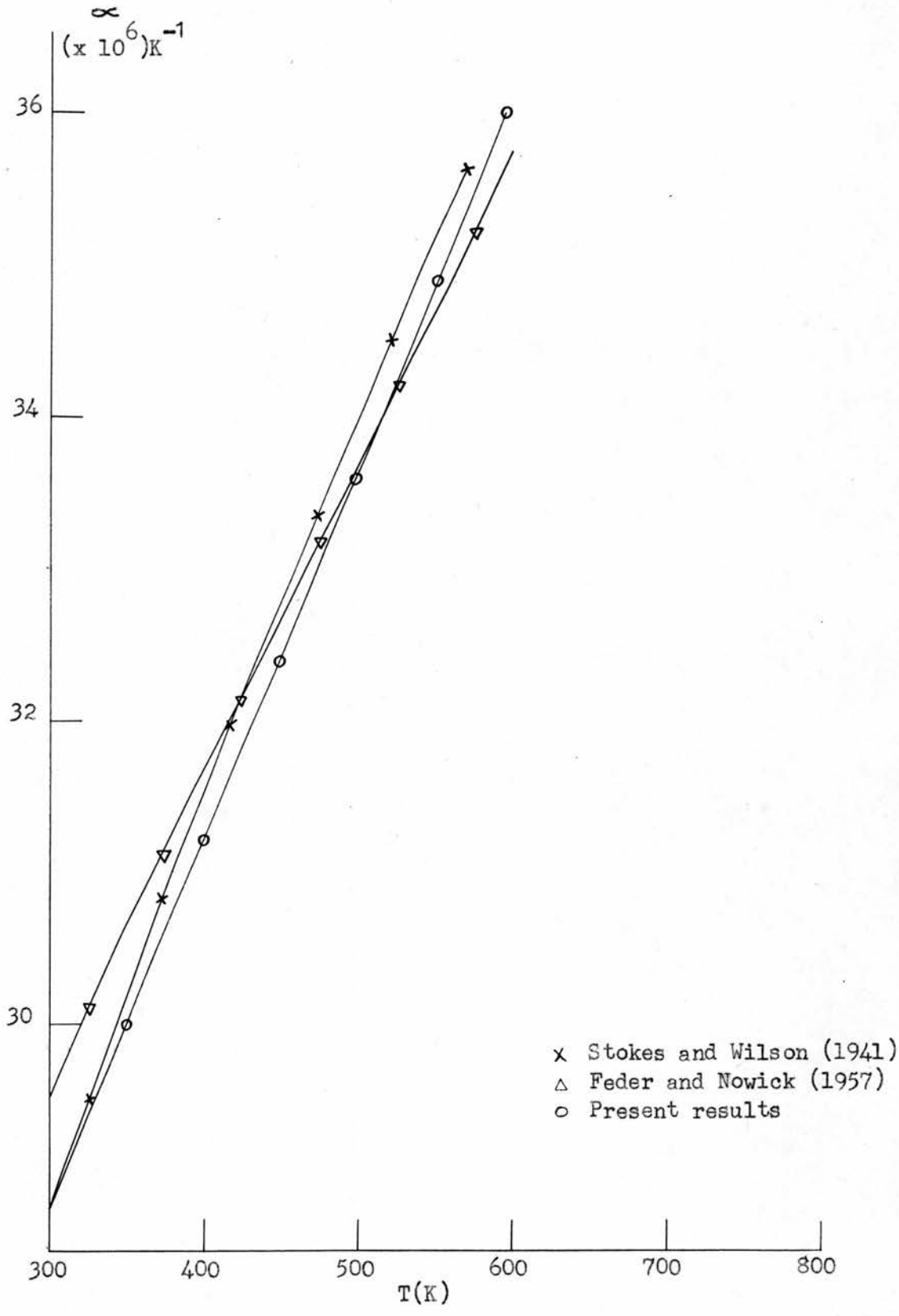


Figure 6 The experimental thermal expansivities of lead compared with the results of other workers.

in figure 6. α was found to vary linearily with temperature as

$$\alpha = \left[(21.14 \pm 0.21) \times 10^{-6} + (25.7 \pm 0.4) \times 10^{-9} T\right] K^{-1}$$

Copper

The thermal expansivities of copper were determined from room temperature up to 850K. Attempts to raise the temperature above 850K were hindered by the formation of a thick oxide layer on the material which could only have been eliminated by evacuating the furnace enclosure. A typical set of results are shown in table 4 and the average results from five runs of modes A and B are listed in table 5 and shown graphically in figure 7. No significant difference in the results of modes A and B were found. In the measured temperature range, α varied linearly with temperature as

$$\alpha = \left[(14.67 \pm 0.09) \times 10^{-6} + (6.98 \pm 0.15) \times 10^{-9} T\right] K^{-1}$$

Aluminium

The thermal expansivities of aluminium from room temperature to the melting point were measured in a similar manner. The results are listed in table 6 and are illustrated on figure 8. The thermal expansivity of aluminium was found to vary non-linearly with temperature and, above 750K, the values of α for mode B were greater than those for mode A.

Discussion of Results

The greatest uncertainties in these determinations of thermal expansivities are associated with the measurements of the temperature rise and of the change in the voltage output of the transducer. The temperature rise was normally restricted to an interval of 50K,

Table 4

Copper - Sample Results

$V = 15.00V$

$Y = 666\ mVV^{-1}cm^{-1}$

$\ell = 1.090$ cm at 293K

$\alpha = (\frac{91.83Y}{t_r} + 0.50 \times 10^{-6})K^{-1}$

T(K)	t_r	mV	y	$\alpha \times 10^6 K^{-1}$	T(K)
300		52.3			
	50		8.9	16.8	325
350		43.4			
	50		9.0	17.1	375
400		34.4			
	50		9.3	17.6	425
450		25.1			
	50		9.5	18.0	475
500		15.6			
	50		9.7	18.4	525
550		5.9			
	50		9.9	18.7	575
600		-4.0			
	50		10.1	19.1	625
650		-14.1			
	50		10.3	19.4	675
700		-24.4			
	50		10.5	19.7	725
750		-34.9			
	50		10.6	20.0	775
800		-45.5			
	50		10.9	20.5	825
850		-56.4			
	50		10.9	20.5	825
800		-45.5			
	50		10.8	20.3	775
750		-34.7			
	50		10.6	20.0	725
700		-24.1			
	50		10.3	19.5	675
650		-13.8			
	50		10.1	19.1	625
600		-3.7			
	50		9.9	18.7	575
550		6.2			
	50		9.7	18.2	525
500		15.9			
	50		9.5	18.0	475
450		25.3			
	50		9.4	17.8	425
400		34.7			
	50		9.0	17.1	375
350		43.7			

Table 5

Copper - Values of Thermal Expansivities (x 10^6)

T(K)	αK^{-1}
325	16.78
373	17.26
425	17.26
475	18.04
525	18.41
575	18.71
625	19.00
675	19.47
725	19.69
775	20.06
825	20.37

Table 6

Aluminium - Values of Thermal Expansivities ($\times 10^6$)

T(K)	αK^{-1}
333	24.02
398	25.01
448	25.98
498	27.10
548	27.83
598	28.94
648	29.80
698	30.86
748	32.28
T(K) Mode A	K^{-1}
798	33.72
848	35.26
898	36.80
T(K) Mode B	K^{-1}
798	34.10
848	36.80
898	39.66

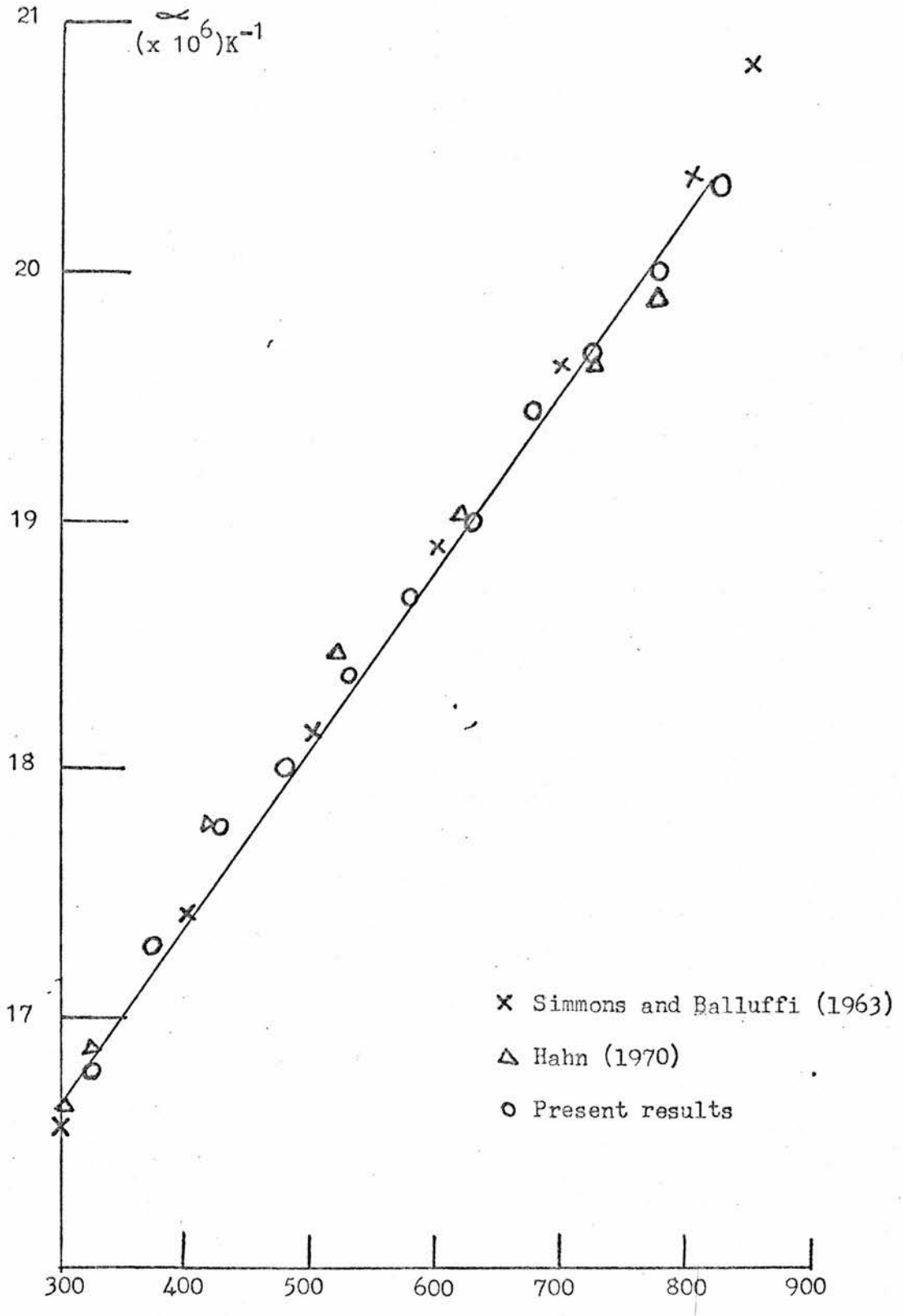


Figure 7 The experimental thermal expansivities of cooper compared with the results of other workers and showing the best straight line through the present results.

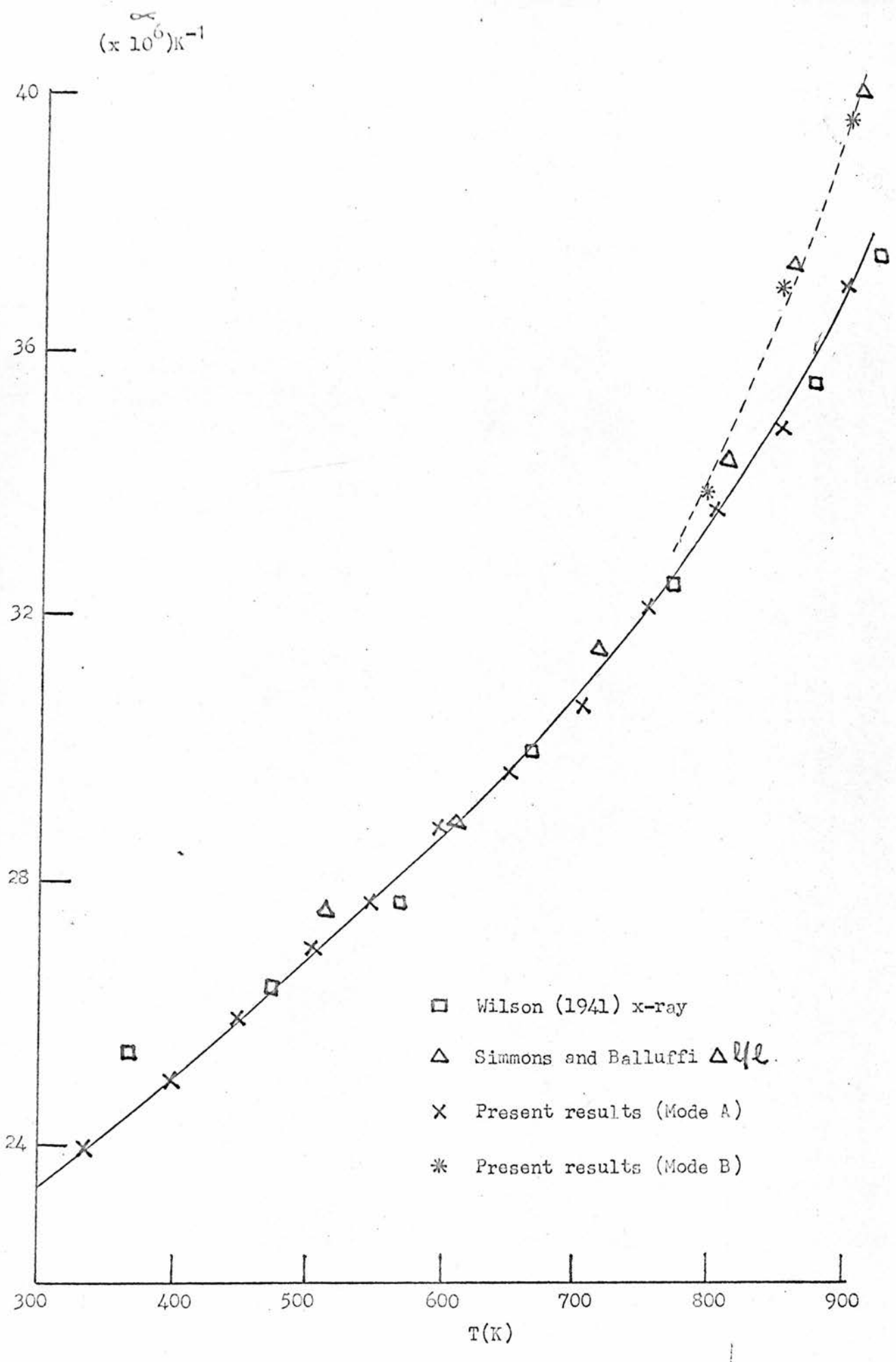


Figure 8 The experimental thermal expansivities of aluminium compared with the results of other workers and showing the high temperature variation of α between mode A and mode B.

being a compromise between detection of variations of the thermal expansivities with temperature and achieving sufficient accuracy from a digital thermometer which could be read to $\pm$ 0.5K. Over a temperature rise of 50K, this gave an accuracy of 1.4% for each individual temperature range. However, since the readings were usually taken five times, an overall accuracy of 0.6% would be expected. The output from the transducer could be read to $\pm$ 0.1 mV and, since the average change in output per temperature interval was approximately 20 mV, an accuracy of 0.3% was expected over the five readings. These two uncertainties, coupled with other less significant errors in the calibration of the transducer, the voltage applied to the transducer and the original length of the samples, suggested that accuracies of less than 0.8% could be claimed. For the substances under investigation this represents the following uncertainties:-

Lead $\pm$ 0.24 x $10^{-6}K^{-1}$ at 300K; $\pm$ 0.28 x $10^{-6}K^{-1}$ at 600K

Copper $\pm$ 0.13 x $10^{-6}K^{-1}$ at 300K; $\pm$ 0.16 x $10^{-6}K^{-1}$ at 825K

Aluminium $\pm$ 0.24 x $10^{-6}K^{-1}$ at 300K; $\pm$ 0.32 x $10^{-6}K^{-1}$ at 825K

The reproducibility of the results for lead given in table 3, suggest an average standard deviation in the mean value at each temperature of $\pm$ 0.08 x $10^{-6}K^{-1}$, (i.e. about 0.3%) which is much smaller than would be expected when the errors in the temperature and voltage reading were considered. During the expansion measurements, the temperature of the samples were kept constant for about 5 minutes, during which time there were very few changes on the digital thermometer and no voltage changes were read unless the reading on the thermometer had remained unchanged for at least one

minute. The error in the temperature reading was therefore probably less than $\pm$ 0.5K.

Lead

Previous investigations into the expansion of lead had been carried out by Stokes and Wilson (1941) and by Feder and Nowick (1957) and are shown in figure 6. Stokes and Wilson determined the thermal expansivity of lead up to its melting point and found the variation of thermal expansivity with temperature to be quite linear and their results were expressed as

$$\alpha = [21.71 \times 10^{-6} + 23.6 \times 10^{-9}T]\ K^{-1}$$

They claimed an accuracy over the temperature range of $\pm$ 0.3 x $10^{-6}K^{-1}$.

Feder and Nowick were concerned with the detection of lattice vacancies and, consequently, they measured the expansion by both x-ray and dilatometric methods. They found no difference between the two expansions, showing a small concentration of vacancies in lead. Their results were presented graphically in the form of fractional increases in the sample size but it was possible to deduce an expression for the thermal expansivity of

$$\alpha = [23.5 \times 10^{-6} + 20.4 \times 10^{-9}T]\ K^{-1}$$

No assessment of accuracy of this expression was possible.

The values obtained by Stokes and Wilson (1941) are not significantly different from those obtained in this work which show a linear variation of thermal expansivity with temperature according to

$$\alpha = [(21.14 \pm 0.21) \times 10^{-6} + (25.7 \pm 0.4) \times 10^{-9}T]\ K^{-1}$$

The agreement between these sets of results, being measured by

x-ray methods and dilatometric results respectively, confirms the results of Feder and Nowick (1957) regarding the low concentration of vacancies in lead.

Copper

Recent thermal expansivity work on copper, above room temperature, has been performed by Hahn (1970) and Simmons and Balluffi (1963). Hahn, using an interferometer, was concerned with the establishing of copper as a standard reference material (S.R.M.) on thermal expansion for the National Bureau of Standards in Washington. Claiming a high degree of accuracy (0.2%), he produced results on expansivity up to temperatures of 850K and the variation of α with temperature was linear as

$$\alpha = \left[15.6 \times 10^{-6} + 5.7 \times 10^{-9} T\right] K^{-1}$$

This figure agreed closely with the work of Simmons and Balluffi in their effort to detect lattice vacancies and may be compared to the present results which gave α to be

$$\alpha = (14.67 \pm 0.09) \times 10^{-6} + (6.98 \pm 0.15) \times 10^{-9} T \quad K^{-1}$$

Taking a temperature of 500K, the value of α for Hahn is $(18.48 \pm 0.04) \times 10^{-6} K^{-1}$ and that for the present investigation is $(18.16 \pm 0.13) \times 10^{-6} K^{-1}$ and these results cannot be considered to be significantly different. All three sets of data are plotted in figure 7.

Aluminium

The thermal expansivities of aluminium have been measured by Simmons and Balluffi (1960a), Feder and Nowick (1957) and Wilson (1941).

The first two of these investigations were concerned with the

detection of lattice vacancies and both observed significant differences between the results obtained by the x-ray method and those of the dilatometer method at temperatures above 750K. For example, Simmons and Balluffi reported at near melting point α(x-ray) to be $(37.0 \pm 0.2) \times 10^{-6} K^{-1}$ while α (macroscopic) to be $(39.2 \pm 0.3) \times 10^{-6} K^{-1}$. These significant differences led them to the conclusion that aluminium had a large vacancy concentration near the melting point and provided sufficient information to deduce the values of the entropy and energy of formation of these defects.

Wilson (1941) measured the expansivities of aluminium by x-ray techniques and his results are shown in figure 8 and used as a comparison with the dilatometer results of Simmons and Balluffi and the present investigation.

Up to 750K, the present values agree with those of Simmons and Balluffi. At higher temperatures, significant differences were noted between expansivities obtained for mode A as for mode B (see table 6). This phenomenon was not reported by Simmons and Balluffi but Feder and Nowick observed that, close to the melting point, an initial expansion was followed by a permanent contraction. This they attributed to creep.

One possible explanation of this phenomenon would be that, since the effect occurs only very close to the melting point, a certain amount of sublimation of the metal would be taking place. During heating, the expansion of the metal could be counteracted to a certain extent by loss of material due to sublimation and thus the net change in length of the sample would be the difference between the changes due to expansion and sublimation. Similarly, during

cooling, the net change in length would be the sum of the changes due to contraction and sublimation. The effect is further enhanced by the experimental technique whereby the sample remains longer at the finishing temperature than the starting temperature and, since it is reasonable to suppose that the greater sublimation takes place at the higher temperatures, there will be less sublimation during cooling and the expansivities measured during a fall in temperature should be more accurate and greater than that measured during a temperature rise. With reference to table 6 it can be seen that the expansivities for a fall in temperature are much closer to the results of Simmons and Balluffi than for a rise in temperature.

This effect would not be observed by Simmons and Balluffi because they did not measure the total length of the sample but considered the distance between two reference marks near the ends of the specimen. Since sublimation would remove material from the surface, this would not affect the distance between the two reference marks.

Close agreement exists between published thermal expansivities and those obtained from the present dilatometer. It can therefore be concluded that the apparatus is sound in design and capable of accurately measuring the variation of thermal expansivities in many materials from room temperature to 1000K. It has the advantages that it is easy to use and relatively cheap to produce. An adaptation of the apparatus, for use in school teaching, is described in Appendix II.

CHAPTER 3

ANALYSIS OF HIGH TEMPERATURE SPECIFIC HEAT DATA

1. Debye Theory

In classical statistical mechanics a solid can be considered to be made up of a system of simple harmonic oscillators of average kinetic energy per degree of freedom $\frac{1}{2}kT$, where k is Boltzmann's constant. Therefore for a gram mole of the substance, having N oscillators, the total internal energy, U, is

$$U = 3NkT$$
$$= 3R$$

where R is the universal gas constant.

The molar specific heat, at a constant volume, C_v, is then 3R

$$\text{i.e. } C_v = 24.977 \text{ J mole}^{-1}\text{K}^{-1}$$

This value is in quite good agreement with the observed heat capacity of many solids at room temperature, but the agreement fails at low temperature since specific heats fall towards zero as the temperature tends to zero. An explanation for this variation of specific heat with temperature cannot be found in classical theory and it requires quantum theory and a knowledge of the possible distribution of frequencies and energies of the atoms in a solid to provide a method of estimating the temperature dependence of specific heat.

The first attempt to account for the low temperature behaviour of specific heat was due to Einstein (1907). In his model a solid is considered to be a system of 3N independent harmonic oscillators,

each having an identical angular frequency, ω. The energies of the oscillators are quantized according to Planck's theory of radiation, such that the energy E may only have the values

$$E = n\hbar\omega$$

where n = 1, 2, 3

and $\hbar = \frac{h}{2\pi}$ where h is Planck's constant.

He then assumed these energies to be distributed according to Boltzmann's distribution law from which the average energy of the oscillation is

$$\bar{E} = \frac{\sum_{n=o}^{\infty} n\hbar\omega \exp(-n\hbar\omega/kT)}{\sum_{n=o} \exp(-n\hbar\omega/kT}$$

and the total energy of the crystal then becomes

$$U = \frac{3N\hbar\omega}{\exp(\hbar\omega/kT)-1}$$

The Einstein specific heat at constant volume, C_v^E, is

$$C_v^E = \left(\frac{\partial U}{\partial T}\right)_v = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 \frac{\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT)-1]^2}$$

At high temperatures, the specific heat agrees with the classical value of 3R and, at lower temperatures, tends to zero as

$$C_v^E = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 \exp(-\hbar\omega/kT)$$

Although this does not quite agree with the experimentally observed T^3 variation, it gives a moderately good fit.

The assumption that all the oscillators have the same frequency is an obvious over-simplification and the exact specific heat can only be calculated provided the distribution of frequencies is known. If we define a frequency distribution $g(\omega)$ such that $g(\omega)d\omega$ is the number of modes having frequencies in the range ω to

$\omega + d\omega$ then the total energy of the crystal is

$$U = \int_0^{\omega_m} \frac{\hbar\omega g(\omega) d\omega}{[\exp(\hbar\omega/kT)-1]}$$

where ω_m is the maximum frequency.

The specific heat at constant volume then becomes

$$C_v = \int_0^{\omega_m} k(\frac{\hbar\omega}{kT})^2 \frac{\exp(\hbar\omega/kT) g(\omega) d\omega}{[\exp(\hbar\omega/kT)-1]^2}$$

and C_v can be determined if $g(\omega)$ is known.

In general, $g(\omega)$ is not a simple function of ω. However, Debye (1912) devised a relatively simple model of a solid and determined a frequency distribution which, although it did not agree very well with experimentally determined distributions, nevertheless gives values of C_v in good agreement with observation, especially at low temperatures. The frequency spectrum used by Debye was that obtained by considering the acoustic spectrum which could be set up in a homogeneous medium. He introduced a maximum frequency ω_m to correspond to the minimum wavelength which would result due to the smallest interatomic spacing of the real solid. Thus

$$g(\omega) = \frac{3\omega^2}{2\pi^2 v_o^3}$$

where v_o is the velocity of sound in the crystal.

The total energy of the crystal is therefore

$$U = \frac{3N\hbar}{2\pi^2 v_o^3} \int_0^{\omega_m} \frac{\omega^3 d\omega}{\exp(\hbar\omega/kT)-1}$$

Debye defined a characteristic temperature for a material, the Debye temperature, Θ using the relationship

$$\hbar\omega_m = k\Theta$$

and, substituting $x = \frac{\hbar\omega}{kT}$ and $x_m = \frac{\hbar\omega_m}{kT} = \frac{\Theta}{T}$,

we have

$$U = \frac{3Nk^4T^4}{2\pi^2\hbar^3v_o^3}\int_o^{x_m}\frac{x^3dx}{\exp(x)-1}$$

which, on differentiating with respect to T, gives the Debye specific heat at constant volume, C_v^D as

$$C_v^D = 9Nk\left(\frac{T}{\Theta}\right)^3\int_o^{x_m}\frac{e^x x^4 dx}{(\exp(x)-1)^2} \quad .. \quad .. \quad (3.1)$$

Figure 9 shows C_v^D plotted as a function of the reduced temperature, T/Θ, and the function has been found to satisfy experimental observations. At high temperatures, the specific heat tends to the classical value of 3R while at low temperatures it gives C_v^D values which are proportional to T^3.

The Debye theory is therefore based on a more realistic model than the Einstein theory and has the great virtue that the Debye specific heat at constant volume is a function of only one parameter, the Debye temperature. This simplification, however, has only been achieved by making two basic assumptions. The distributions of the frequency modes is taken to be that of acoustic waves in the solid, and the motion of the oscillators is harmonic. Since the Debye theory is in such common use it is of great importance to test how closely real materials obey the theory. Experiments show that measured frequency distributions are usually quite different to that predicted by the Debye theory and, since all materials have a thermal expansivity, the harmonic approximation, on which the Debye theory is based, is invalid.

The values of specific heats obtained from the Debye theory cannot be verified directly by experiment since it would be extremely difficult to measure with any degree of accuracy the specific heat

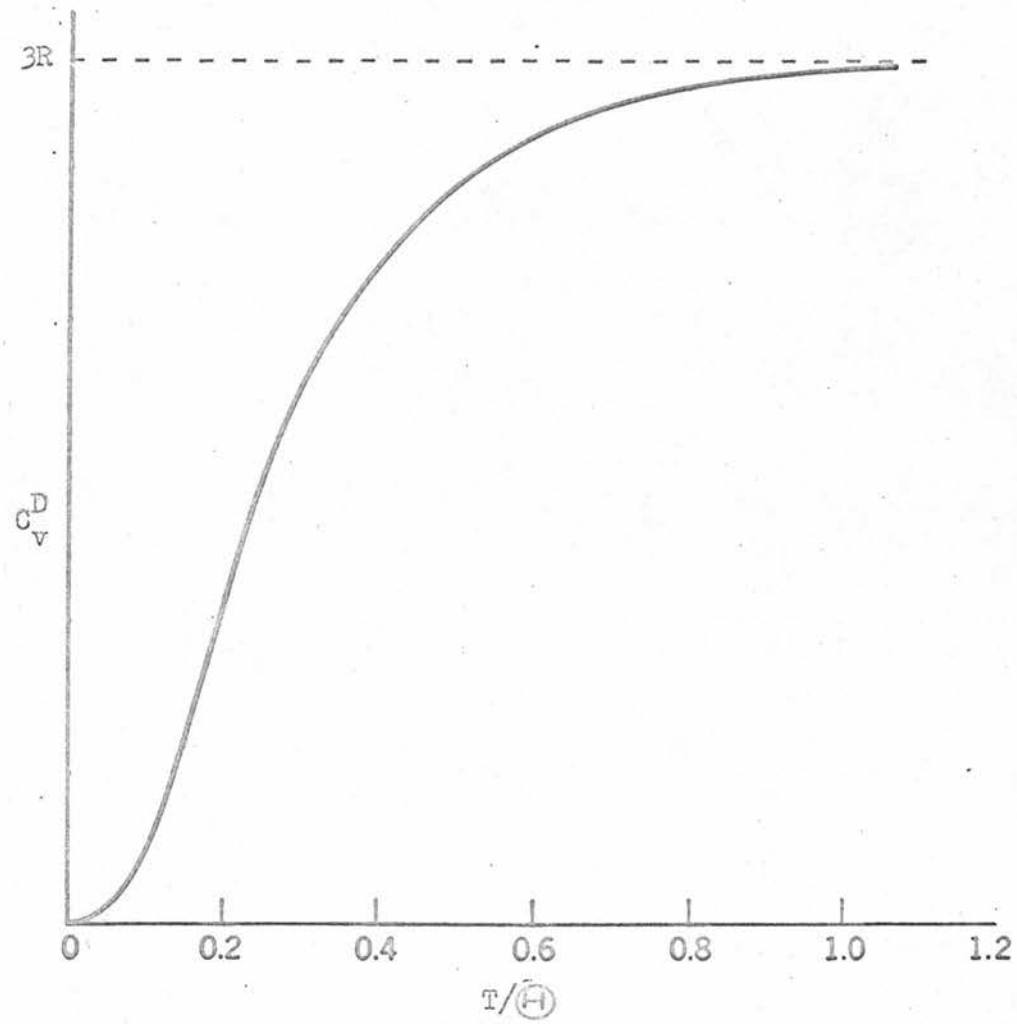


Figure 9 The specific heat at constant volume of a Debye solid as a function of reduced temperature.

at constant volume of a solid. Experimental measurements of specific heats are always made at constant pressure and therefore yield values of the specific heat at constant pressure, C_p.

The contribution to the specific heat at constant pressure due to the expansion of the material, which will be referred to as the dilation effect, C_x, can easily be determined. However, during experimental determinations of C_p, a certain amount of energy is given to the free electrons and used in the formation of lattice defects giving contributions of C_E and C_D respectively to C_p. A comparison of the specific heat at constant volume of a substance and its Debye specific heat can only be made if all those effects are taken into account. If the excess specific heat, ΔC_v, is defined as the difference between the real specific heat at constant volume, C_v, and the Debye specific heat, then values of ΔC_v can be calculated from experimental C_p values using

$$\Delta C_v = C_v - C_v^D$$

$$= C_p - C_v^D - C_x - C_E - C_D \quad .. \quad .. \quad (3.2)$$

Each term in the above equation is dependent on the experimental measurement of at least one physical quantity and physically meaningful values of excess specific heats can only be obtained by a thorough analysis of all the available experimental values of these parameters which occur in each of the terms.

2. Experimental Determination of Specific Heat at Constant Pressure

In the experimental determination of the specific heat of a material, the material must be supplied with a measurable amount of heat and the corresponding rise in temperature measured. As the

temperature of the material rises, it will lose heat to its surroundings and the amount of heat lost will be very difficult to determine. This problem can be overcome by controlling the environment in such a way that the process may be considered to be either isothermal or adiabatic.

In the isothermal method, the calorimeter is surrounded by an outer jacket which is maintained at a constant temperature thus making it possible to calculate heat losses. While this method is very easy to use, it is not suitable for high temperatures because of the high rates of radiation heat transfer which introduce large errors.

Most recent experiments have employed the adiabatic method in which the calorimeter is surrounded by an outer jacket maintained at the same temperature as the calorimeter. This condition can be achieved by use of a thermocouple, in conjunction with automatic controlling devices. The adiabatic calorimeter is the more accurate and a typical example of this apparatus has been described by Stansbury, McIlroy, Picklesimer, Elder and Pawel (1959) and modified by Stansbury, Nauman and Brooks (1965).

The specimen, in the form of a polished cylinder, is suspended inside a closed metal cylinder which acts as a main adiabatic shield. This shield is heated by a bare metal wire controlled by a system of thermocouples to maintain the specimen and shield at the same temperature. The system is evacuated to a pressure of 10^{-5} Torr to eliminate convectional heat transfer and oxidation and the adiabatic shield is surrounded by a granular refractory and a water cooled outer jacket to avoid temperature fluctuations and gradients. A heater is placed in a hole in the centre of the specimen and the

power leads brought up through the specimen wall to establish good thermal equilibrium. By measuring the time taken to raise the temperature of a known weight of specimen through a predetermined temperature range, the power to the specimen heater can be calculated and hence the average specific heat of the specimen determined.

A correction is made to this apparent specific heat to account for the difference between the specific heat of the specimen and that of the heater. This correction is minimised by making the heater very small and keeping its heat capacity below 1% of that of the specimen. For materials having specific heats near that of copper, the error introduced by adding the heater mass to the specimen mass is 0.1%.

A further correction is necessary to account for the deviation from adiabatic conditions. The apparent specific heat, C_p^a, was calculated, usually over a 20K temperature interval, from

$$C_p^a = \frac{EI\Delta t}{m\Delta T}$$

where E = mean heater voltage

I = current

t = time

T = temperature interval

m = mass

Inevitably some heat is lost from the specimen and a correction factor, applied to the apparent specific heat, has been derived by Pawel (1956) to obtain the experimental specific heat, C_p.

$$C_p = \frac{C_p^a}{1-(C_p^a - R/K)}$$

where R is a measure of the rate at which the temperature of the specimen falls at a particular temperature and K is the power input to the specimen.

Brooks, Noram, Hendrix, Wright and Northcott (1968) produced a further modification of this apparatus to measure the specific heat at constant pressure of copper, aluminium and gold, and values for aluminium and lead have been obtained using a similar apparatus by Leadbetter (1968). These latter determinations have been quoted by the author to better than 1% but, as will be shown later, significant differences between determinations of the same substance exist.

3. Debye Specific Heat

The Debye specific heat of a material is a function only of the Debye temperature which was related by Debye to the maximum vibration frequency, ω_m by

$$\Theta_D = \frac{\hbar \omega_m}{K}$$

The Debye temperature, Θ_D, is thus defined as a function of the maximum frequency, but relating Θ_D to measurable physical quantities requires the averaging of the complete frequency distribution. The various methods of equating the physical properties to Θ_D tend to use different methods of averaging and different approximations resulting in slightly differing estimates of the Debye temperature. The more common methods of determining Θ_D are based on measurements of (a) elastic constants (Blackman, 1955), (b) low temperature specific heats and (c) Debye-Waller factors (Debye, 1914; Waller, 1923). Using these three methods the Θ_D values for copper have been determined at room temperature. They are respectively 332K, 310K and 308K (Gschneidner, 1964).

Since both the maximum frequency and the frequency distribution

vary with temperature, the Debye temperature will also be a function of temperature and studies on Cu, Pb, Au, Ag and Al suggest that Θ_D decreases slowly with increasing temperature.

The Debye specific heat is obtained by substituting the Debye temperature in the Debye function as in equation (3.1). At temperatures greater than the Debye temperature, the Debye function varies very slowly with temperature and any uncertainties in Θ_D give rise to small changes in the Debye specific heat. For example, with reference to copper from the three methods mentioned above, the variation in the Debye specific heat is no more than 0.2% at 600K.

4. Dilation Term

During an experimental determination of the specific heat at constant pressure some of the energy given to the solid is used to increase the volume of the sample. The specific heat at constant volume, C_v, can be deduced from the specific heat at constant pressure, C_p, using the well-known thermodynamic relation,

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_V$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial P}{\partial V}\right)_T$$

Volume thermal expansivity, $B = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal Compressibility $K_I = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\therefore C_p - C_v = \frac{TVB^2}{K_I}$$

$$= \frac{9\alpha^2 TV}{K_I}$$

since $B = 3\alpha$ and α is the linear expansivity.

Thus $C_p - C_v = C_x = \frac{9\alpha^2 TV}{K_I}$ .. .. (3.3)

where V is the specific volume. In this derivation it is assumed that no electronic or vacancy formation effects are present.

The dilation contribution, C_x, can therefore be determined provided values of α, V and K_I are available over the required temperature range. The determination of the thermal expansivities, α, has already been described. Very accurate values of V are readily available from density measurements at one temperature, usually room temperature, to which corrections for expansion can be applied. Compressibility experiments usually yield values of the adiabatic compressibility, K_s, from which the isothermal compressibility can be determined. It can be shown that (Zemansky, 1957)

$$K_I = K_s + \frac{9\alpha^2 VT}{C_p}$$

The adiabatic compressibilities are obtained from measurements of the velocities of sound waves in the principal direction in the material which yield values of the elastic moduli in these directions.

The magnitude of C_x ranges from about 5% of the C_p value at room temperature to as much as 20% for a material of high melting point. Errors of 1% in both α and K_I should therefore not significantly affect the overall analysis.

5. Electronic Specific Heat

According to the free electron model of a metal, the valence electrons of the constituent atoms of the metal are able to move freely through the volume of the solid and classical statistical mechanics predicts that a free point particle should have a heat

capacity of $\frac{3}{2}k$. If N atoms each give one valence electron, then the electronic contribution to the heat capacity should be $\frac{3}{2}Nk - \frac{3}{2}R$, making a total specific heat at constant volume

$$C_v = 3R + 1.5R = 4.5R$$

This is far higher than any measured specific heat and the contribution from the electrons must be much less than that deduced from classical theory.

The introduction of the Pauli exclusion principle in conjunction with Fermi-Dirac statistics provided an understanding of the small contribution given to the specific heats of metals by electronic effects. According to Fermi-Dirac statistics, the probable number N_k particles in energy state ϵ_k is

$$N_k = \frac{g_k}{\exp[(\epsilon_k - \epsilon_F)/kT] + 1}$$

where

g_k = number of levels with energy ϵ_k

ϵ_F = Fermi energy level

Thus the probability that a particular state is occupied is given by the Fermi Dirac distribution function

$$f(\epsilon) = \frac{1}{\exp[(\epsilon - \epsilon_F)/kT] + 1}$$

As $T \rightarrow 0$, $f(\epsilon)$ is unity for any energy less than ϵ_F and then abruptly drops to zero for $\epsilon > \epsilon_F$. In other words, all the energy states below ϵ_F are fully occupied, while all the states above ϵ_F are empty.

Therefore on heating from absolute zero, with quantum restrictions it can be seen that not every electron gains in energy kT, but only

those within the energy range kT of the Fermi level are thermally excited.

This modification of the thermal properties of the conduction electrons gives an immediate qualitative solution to the problem of the heat capacity. If n is the total number of free electrons per atom, only a fraction, of the order of T/T_F, where T_F is the Fermi temperature and is defined as $\epsilon_F = kT_F$, can be excited thermally at a temperature T since only these lie within kT of the top of the energy distribution. Each of these nNT/T_F electrons has a thermal energy of kT and so the total electronic thermal energy, E_E, is of the order of

$$E_E = \frac{nNT}{T_F} kT$$

The electronic heat capacity is therefore

$$C_E \approx \frac{d(E_E)}{dT} \quad \frac{nNkT}{T_F}$$

As stated earlier, the contribution of the electronic specific heat to the lattice specific heat is very small at room temperatures. However at sufficiently low temperatures, the lattice specific heat decays as T^3 towards zero, and the electronic specific heat decays linearly with T. This means that ultimately the C_E must dominate C_v and in typical metals this may be expected to occur at below 1OK. This dominance allows experimental values of electronic specific heat to be measured at low temperatures and the total heat capacity at a constant volume may be written as

$$C_v^{Total} = \gamma T + AT^3$$

where γ = electronic heat constant

and, from the Debye theory, $A = \frac{12\pi^4 NK}{5\Theta^3}$

Parkinson (1958) has shown that for a temperature much less than the Fermi temperature,

$$\gamma T = \frac{4\pi^2 mk^2}{3h^2} \left(\frac{3NV^2}{\pi}\right)^{\frac{1}{3}} T$$
$$= 1.36 \times 10^{-4} V^{\frac{2}{3}} n^{\frac{1}{3}} T \text{ J mol}^{-1}\text{K}^{-2}$$

where n = number of electrons per atom.

The values of γ obtained from the above equation are of the same order of magnitude as those obtained experimentally but the agreement is not entirely satisfactory, in each case the experimental value is greater than the theoretical. The experimental values are those quoted by Gschneidner (1964).

	n	V	γ ($\times 10^4$) (theoretical)	γ ($\times 10^4$) (experimental)
Cu	1	7.09	5.02	6.93
Al	3	9.99	9.11	13.06
Au	1	10.21	6.41	7.49
Ag	1	10.27	6.43	6.60
Pb	4	18.34	15.05	31.40

There are two possible reasons for the significant differences between experimental and theoretical values. The first is that the experimental values are determined at low temperatures and extrapolated to higher temperatures, where the variation of γ with temperature may not be linear. Another possible explanation was put forward by Buckingham and Schaforth (1954), who suggested that the specific heat is enhanced at low temperatures by electron phonon interactions but it is unlikely that this effect could account for the large discrepancies which exist between theoretical and experimental values in some elements, for example, lead and aluminium.

Various experimental determinations of γ suggest that the errors in γ are quite small ($\pm$ 2%) and, since the electronic contributions to the specific heat is usually less than 1J $mol^{-1}K^{-1}$, the corresponding error in ΔC_v will be very small provided these experimental values do actually represent the correct electronic contribution at higher temperatures.

6. Effect of Vacancy Formation

In Chapter 2 reference was made to the presence of defects in crystals and their effect on some physical properties. Upon raising the temperature of a sample, the defect concentration increases to a new equilibrium value and in so doing the material absorbs energy. This energy absorption causes a rise in heat capacity. For the purpose of this work attention will be centred only on the formation of monovacancies as they are the most common defects present in simple metal crystals.

Equation (2.3) gives a measure of the concentration of vacancies present at a temperature T and the total energy required to produce these defects will be

$$E_D = nW$$

where W is the energy of formation of the defect

and n is the number of defects per gram mole.

The contribution to the heat capacity of the formation of these monovacancies is given by

$$C_D = \frac{d E_D}{d T} = \frac{nW^2}{kT^2} \exp(\Delta S/k) \exp(-W/kT) \quad .. \quad (3.4)$$

7. Some Determinations of Excess Specific Heat

The excess specific heats have been determined from the equation

$$\Delta C_v = C_p - C_v^D - C_x - C_E - C_D$$
$$= C_p - C_v^D - \frac{9\alpha^2 TV}{K_I} - \gamma T - \frac{nW^2}{kT^2}\exp(\Delta S/k)\exp(-W/kT)$$

and ΔC_v is to be considered as the difference between the specific heat at constant volume and the Debye specific heat and its value will reflect any discrepancies in the Debye theory.

The working equation for the determination of the excess specific heat contains many physical quantities whose values can only be obtained from experiment. There exist extensive experimental data for five face centred cubic metals, Pb, Al, Cu, Ag and Au, enabling an analysis of these substances to be carried out. For most of the physical quantities required, more than one recent determination is available and in some cases significantly different values of the same physical parameter have been reported.

The largest two terms in the equation are C_v^D and C_p. As has already been mentioned, although the errors in the Debye temperature may be large, the errors in the corresponding Debye function are sufficiently small so that no significant errors in C_v^D occur. However the C_p values did differ significantly, in some cases the difference between the values quoted was greater than the expected excess specific heats necessitating an analysis to be made for all recently determined C_p data sets.

The other possible errors associated with the working equation are of less significance. Errors in the dilation term would originate from the reported experimental data on thermal expansivities

and compressibilities and determinations of thermal expansivity were found, in some cases, to differ significantly. However these uncertainties were partially resolved by employing data obtained from x-ray diffraction which, as mentioned in Chapter 2, requires no correction for vacancy formation. Compressibility experimental values of the materials in question have been reported for temperatures well short of the melting point and as a consequence they have had to be extrapolated. This results in a further increase in the uncertainties.

Uncertainties could also arise from the values of the electronic constants used. In general, the experimental values were employed but, in the case of Pb and Al , where there were large discrepancies between γ experimental and γ theoretical, the analysis was carried out for both values. The contribution of the vacancy term is usually sufficiently small that errors in W and $\Delta S/k$ only have a small effect close to melting point.

In addition to the individual C_p data sets for the five metals, there also exists data sets of Hultgren, Orr, Anderson and Kelly (1963) compiled by averaging results from earlier experiments. These sets have also been analysed, although no estimate of error can be made for these results.

Before embarking on a detailed investigation of the excess specific heats of the five face centred metals, it is worth noting that theoretical investigations into specific heat at constant volume and its variation with temperature are sufficiently complicated to have been restricted to simple close packed crystals. Such calculations have been made by Leibfried and Ludwig (1961) and Maradudin, Flinn and Caldwell-Horsfall (1961) and they have suggested

the specific heat at a constant volume can be written in the form

$$C_v = 3R(1 + AT + BT^2 + ...)$$

Since $$C_v = C_p - C_x - C_D - C_E$$

and, at temperatures greater than the Debye temperatures,

$$C_v^D = 3R$$

we have $$\Delta C_v = C_v - C_v^D$$

$$= C_v - 3R$$

$$= 3R(AT + BT^2)$$

$$= A'T + B'T^2$$

To a first approximation the excess specific heat can therefore be expected to vary linearly with temperature and it has been further suggested that A' would be negative. This result has been confirmed by Leadbetter (1968b) for aluminium and lead but conflicting results showing positive values of A' have been reported for copper, aluminium and gold by Brooks (1968), Brooks and Bingham (1968) and Cordoba and Brooks (1971) respectively.

The following section describes the determination of the excess specific heats for all five metals at intervals of 50K from 300K to the melting temperature for each substance. The values of the specific heats at a constant pressure and the thermal expansivities at these temperature intervals were determined by three point interpolation of the published experimental results. The values of the adiabatic compressibilities were determined similarly except when the high temperature data was unavailable, in which case values up to the melting point were obtained from extrapolation. The

calculations were done on an IBM 1130 computer. The outputs from the computer are to be found in the Appendix showing the individual terms of equation (3.2) at temperature intervals of 50K together with the values of the Grüneisen "constant".

The ΔC_v values for the five metals are shown graphically in figures 11, 13, 14, 16, 18 and 20. The values of ΔC_v, calculated at intervals of 50K, from 300K to melting point have been joined by smooth curves but it is not suggested that these curves indicate the true variation of excess specific heat with temperature and in some cases a linear variation is suggested in the text.

Lead

C_p (a) Leadbetter (1968a), $\pm$ 0.2%

(b) Cordoba and Brooks (1971a), $\pm$ 1%

(c) Hultgren et al (1963), $\pm$ 0.1%

α Stokes and Wilson (1941), $\pm$ 1%

K_a Waldorf and Alers (1962), $\pm$ 3%

$W = (0.50 \pm 0.02)$eV (D'Heurle, Feder and Nowick, 1965)

$\Delta S/K = (1.5 \pm 0.5)$ (D'Heurle, Feder and Nowick, 1965)

$\gamma_x = (3.14 \pm 0.04) \times 10^{-3}$ J mol^{-1}K^{-2} (Gschneidner, 1964)

$\gamma_t = 1.50 \times 10^{-3}$ J mol^{-1}K^{-2}

$\Theta = (102 \pm 5)$ K (Gschneidner, 1964)

Error in ΔC_v (a) $\pm$ 0.10 at 300K to $\pm$ 0.22 J mol^{-1}K^{-1} at melting point

(b) 0.26 at 300K to $\pm$ 0.35 J mol^{-1}K^{-1} at melting point

(c) 0.26 at 300K to 0.34 J mol^{-1}K^{-1} at melting point

The experimental data sets (a) and (b) do not differ significantly and are very similar to set (c). The excess specific heat values were always negative and varied linearly with temperature as

$$\Delta C_v = -(3.3 \pm 0.7) \times 10^{-3} T \text{ J mol}^{-1}\text{K}^{-1} \quad (\gamma \text{ exp})$$

compared with

$$\Delta C_v = -(4.0 \pm 1.0) \times 10^{-3} T \text{ J mol}^{-1}\text{K}^{-1}$$

obtained by Leadbetter (1968b) using data set (a) and with the theoretical electronic constant sets (b) and (c) give the approximate relation

$$\Delta C_v = -(1.8 \pm 0.7) \times 10^{-3} T \text{ J mol}^{-1}\text{K}^{-1}$$

The C_p data sets and the calculated ΔC_v are shown graphically in figures 10 and 11 respectively.

Aluminium

C_p (a) Leadbetter (1968a), $\pm$ 0.2%

(b) Brooks and Bingham (1968), $\pm$ 0.7%

(c) Hultgren et al (1963), $\pm$ 0.1%

α Simmons and Balluffi (1960b)

K_a Gerlich and Fisher (1968)

$W = (0.75 \pm 0.01)$eV (Simmons and Balluffi, 1960b)

$\Delta S/K = (2.2 \pm 0.2)$ (Simmons and Balluffi, 1960b)

$\gamma_x = (1.36 \pm 0.01) \times 10^{-3}$ J mol^{-1}K^{-2} (Gschneidner, 1964)

$\gamma_t = (0.911) \times 10^{-3}$ J mol^{-1}K^{-2}

$\Theta = (423 \pm 5)$ K (Gschneidner, 1964)

Error in ΔC_v (a) $\pm$ 0.2 at 300K to $\pm$ 0.15 J mol^{-1}K^{-1} at melting point

(b) $\pm$ 0.28 at 300K to $\pm$ 0.25 J mol^{-1}K^{-1} at melting point

(c) $\pm$ 0.28 at 300K to $\pm$ 0.37 J mol^{-1}K^{-1} at melting point

The C_p values (a) and (b) were significantly different, set (a) being in all cases greater than (b) by 0.27 J mol^{-1}K^{-1} (1.1%) at

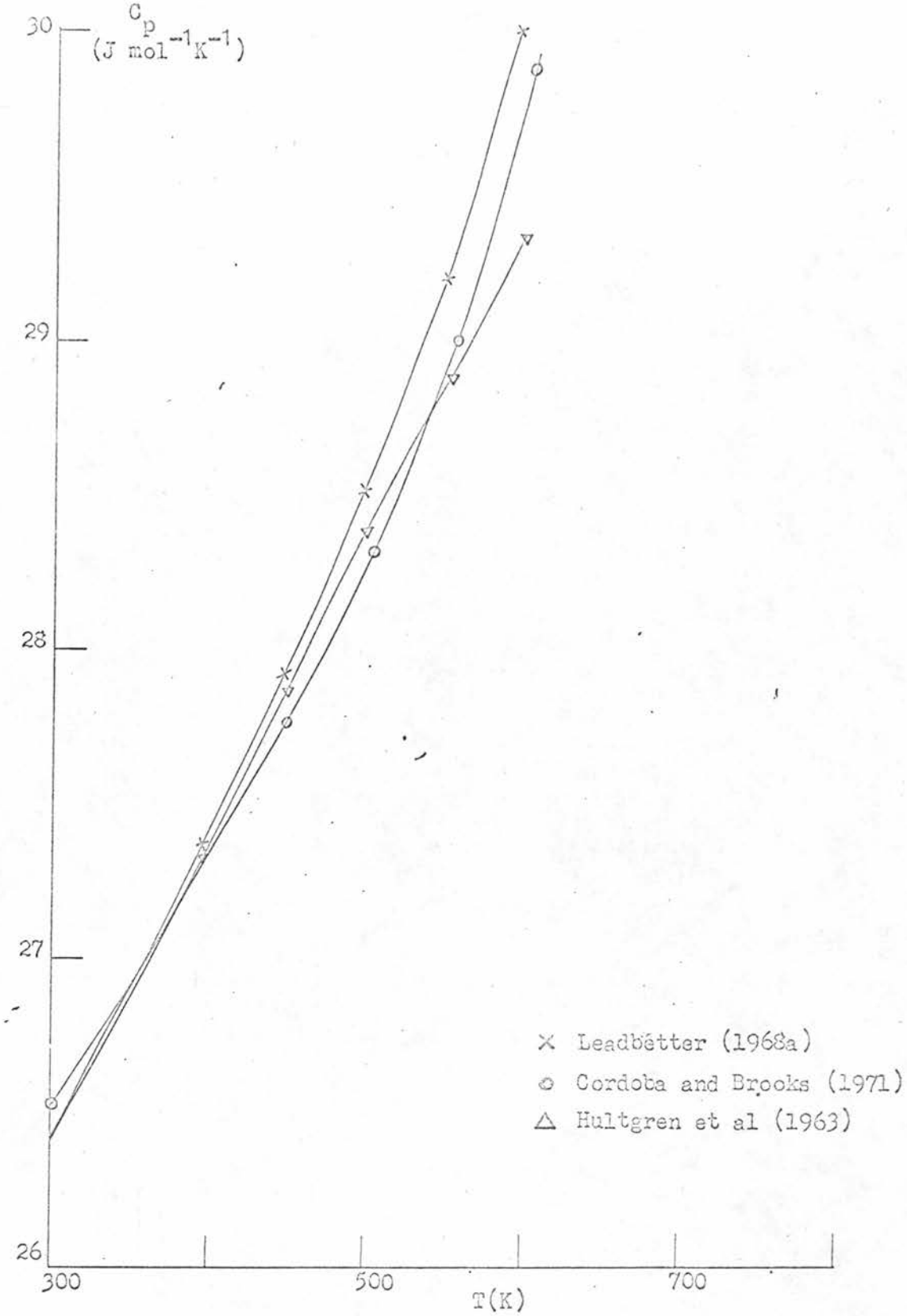


Figure 10 The experimental specific heats of lead used in the analysis.

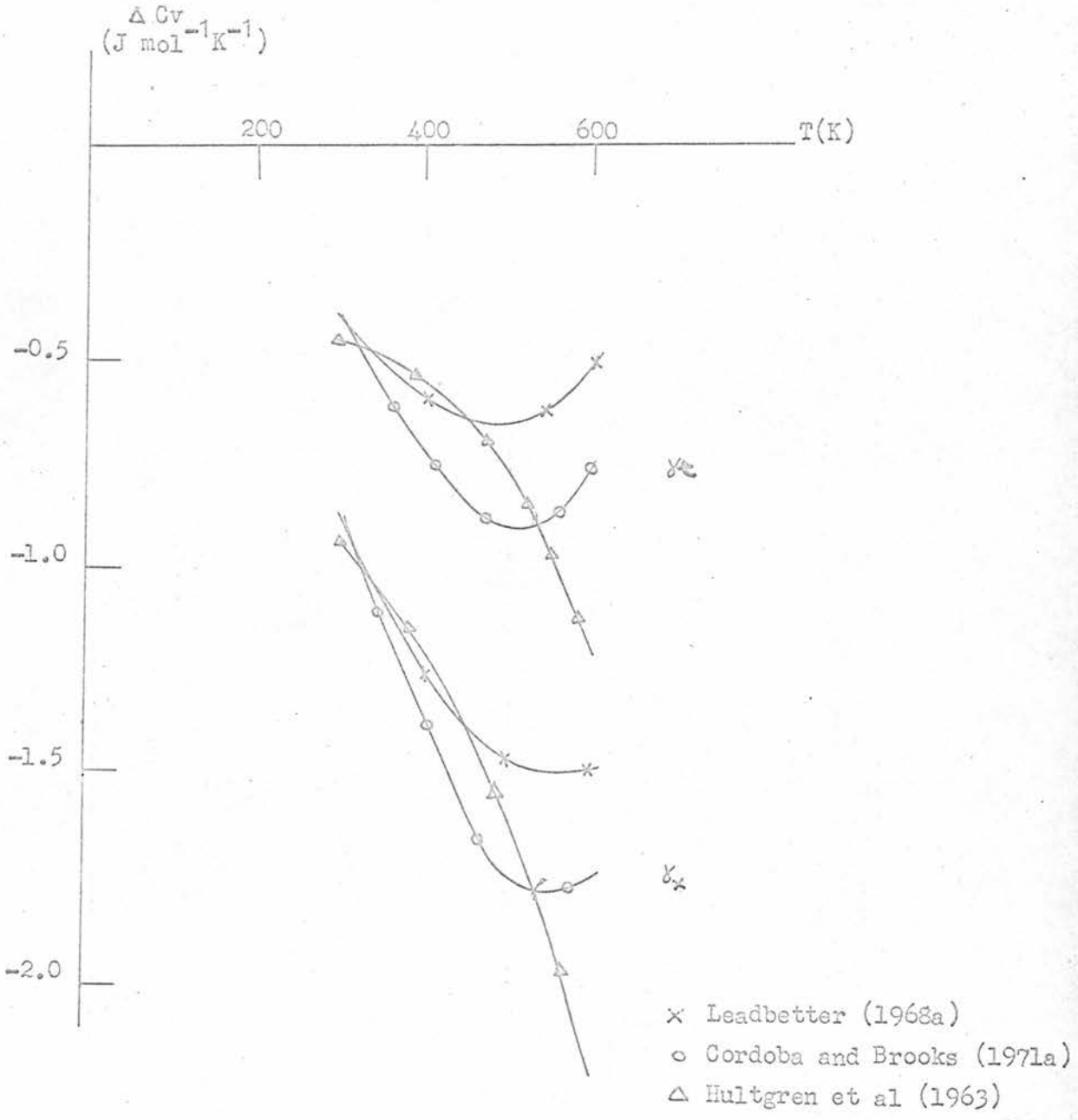


Figure 11 The excess specific heats for lead using both theoretical and experimental electronic specific heat constants.

300K and 1.61 J $mol^{-1}K^{-1}$ (5.2%) at 772K, the highest temperature reached in the Leadbetter experiment. Very different values of the excess specific heats were obtained from the analysis of these sets and it must be concluded that one of the sets was subject to systematic error.

Obviously no conclusion could be reached as to the correct values of ΔC_v. Very approximate linear relationships of

$$\Delta C_v = -(0.9 \pm 0.3) \times 10^{-3} T \text{ J mol}^{-1}\text{K}^{-1}$$

and $$\Delta C_v = (0.6 \pm 0.3) \times 10^{-3} T \text{ J mol}^{-1}\text{K}^{-1}$$

were obtained for (a) and (b) respectively, the equation for (a) agreeing with that of Leadbetter (1968b). The data set of Hultgren et al (1963) gave no significant values for ΔC_v if a 1% error in their data is assumed.

The C_p data sets and the calculated ΔC_v's are shown in figures 12, 13 and 14 respectively.

Copper

C_p (a) Vollmer and Kohlhaas (1968), $\pm$ 2%

(b) Brooks et al (1968), $\pm$ 0.7%

(c) Hultgren et al (1963), $\pm$ 1%

α Simmons and Balluffi (1963), $\pm$ 1%

K_a Chang and Himmel (1966), $\pm$ 2%

W = (1.0 $\pm$ 0.1)eV (Simmons and Balluffi, 1962a)

$\Delta S/K$ = (1.5 $\pm$ 0.5) (Simmons and Balluffi, 1962a)

γ_x = (0.693 $\pm$ 0.007) x 10^{-3} J $mol^{-1}K^{-2}$ (Gschneidner, 1964)

Θ = (342 $\pm$ 2) K (Gschneidner, 1964)

Error in ΔC_v (a) $\pm$ 0.5 at 300K to $\pm$ 0.76 J $mol^{-1}K^{-1}$ at melting point

(b) $\pm$ 0.2 at 300K to $\pm$ 0.4 J $mol^{-1}K^{-1}$ at 1200K

(c) $\pm$ 0.3 at 300K to $\pm$ 0.5 J $mol^{-1}K^{-1}$ at melting point

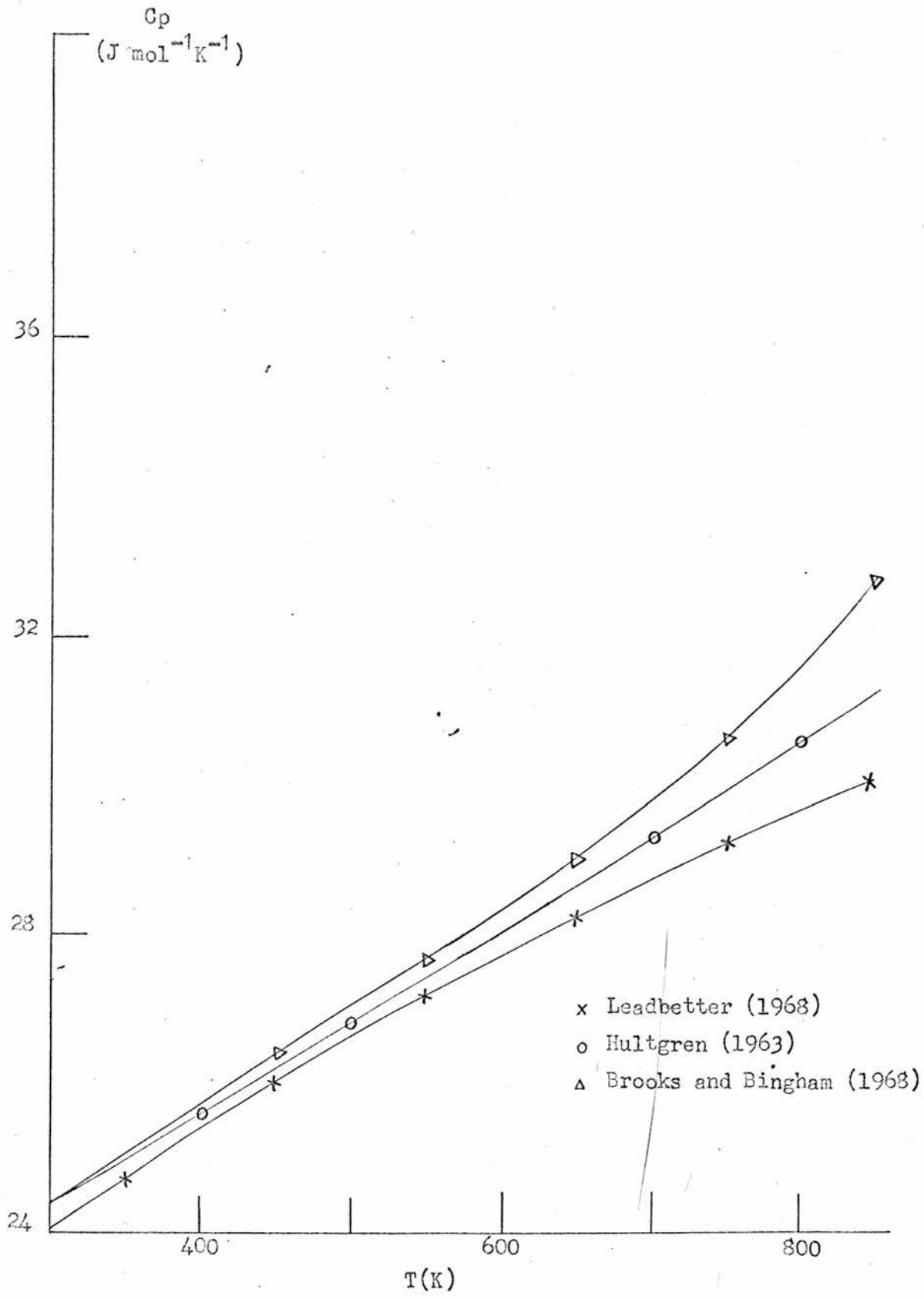


Figure 12 The experimental specific heats of aluminium used in the analysis.

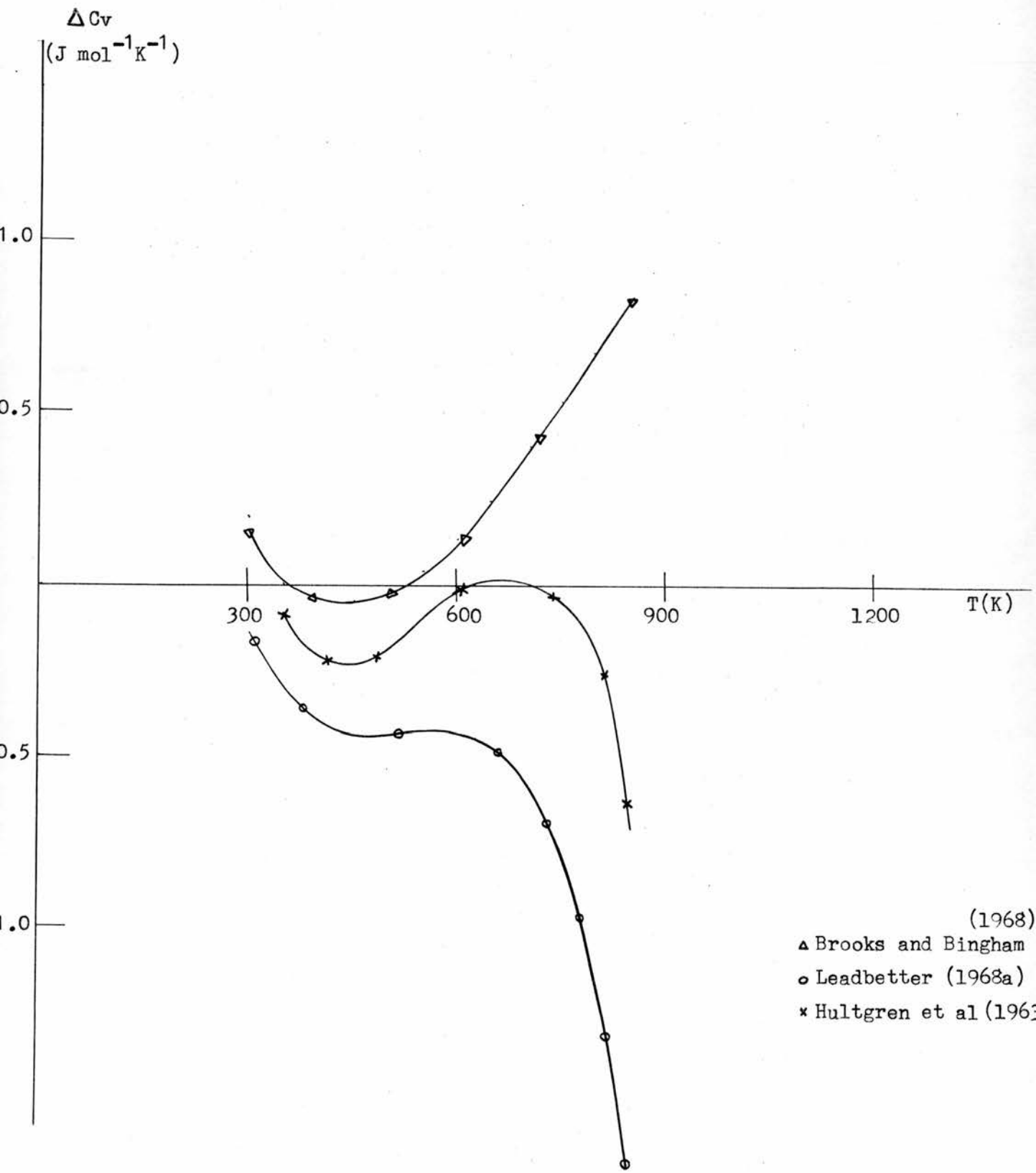


Figure 13 The calculated excess specific heats of aluminium using the experimental electronic heat constant.

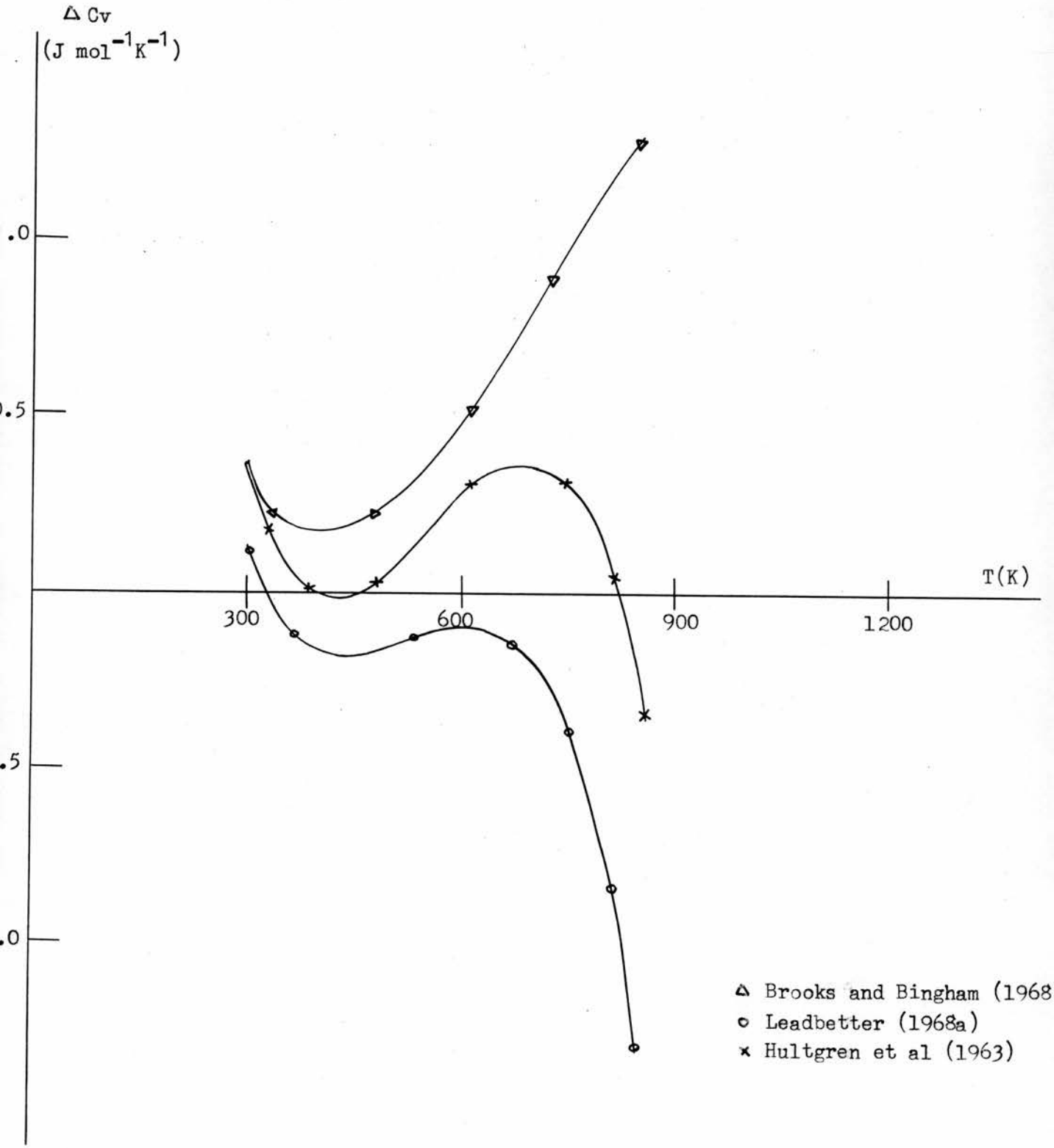


Figure 14 The excess specific heat of aluminium using the theoretical electronic heat constant.

The C_p values (a), (b) and (c), shown in figure 15 agree well up to 1000K with a divergence of 3% occuring at 1200K between (b) and (c), the maximum temperature quoted for set (b). Data set (a) gives no significant excess specific heat over the whole temperature range and the set of Hultgren et al (1963) follows the values of set (a) very closely, never differing from it by more than 0.3 J $mol^{-1}K^{-1}$. The excess specific heat obtained from data set (b), however, increases fairly uniformly from zero at 300K to 0.7 J $mol^{-1}K^{-1}$ at 1200K according to the approximate relation

$$\Delta C_v = (0.4 \pm 0.2) \times 10^{-3} T \text{ J mol}^{-1}\text{K}^{-1}$$

The excess specific heat is shown in figure 16.

Silver

C_p (a) Vollmer and Kohlhaas (1968), $\pm$ 2%

(b) Hultgren et al (1963) $\pm$ 1%

α Simmons and Balluffi (1960a), $\pm$ 1%

K_a Chang and Himmel (1966), $\pm$ 2%

$W = (1.09 \pm 0.1)$eV (Simmons and Balluffi, 1960a)

$\Delta S/K = (1.5 \pm 0.5)$ (Simmons and Balluffi, 1960a)

$\gamma_x = (0.66 \pm 0.03) \times 10^{-3}$ J $mol^{-1}K^{-2}$ (Gschneidner, 1964)

$\Theta = (228 \pm 3)$ K (Gschneidner, 1964)

Error in ΔC_v (a) 0.48 at 300K to 0.7 J $mol^{-1}K^{-1}$ at melting point

(b) 0.25 at 300K to 0.4 J $mol^{-1}K^{-1}$ at melting point

The excess specific heat was about -0.6 J $mol^{-1}K^{-1}$ at 300K, increasing to zero at 850K and remaining at that value up to the melting point. Due to the relatively large uncertainty in the C_p values, it was concluded that no excess specific heat had been detected for silver.

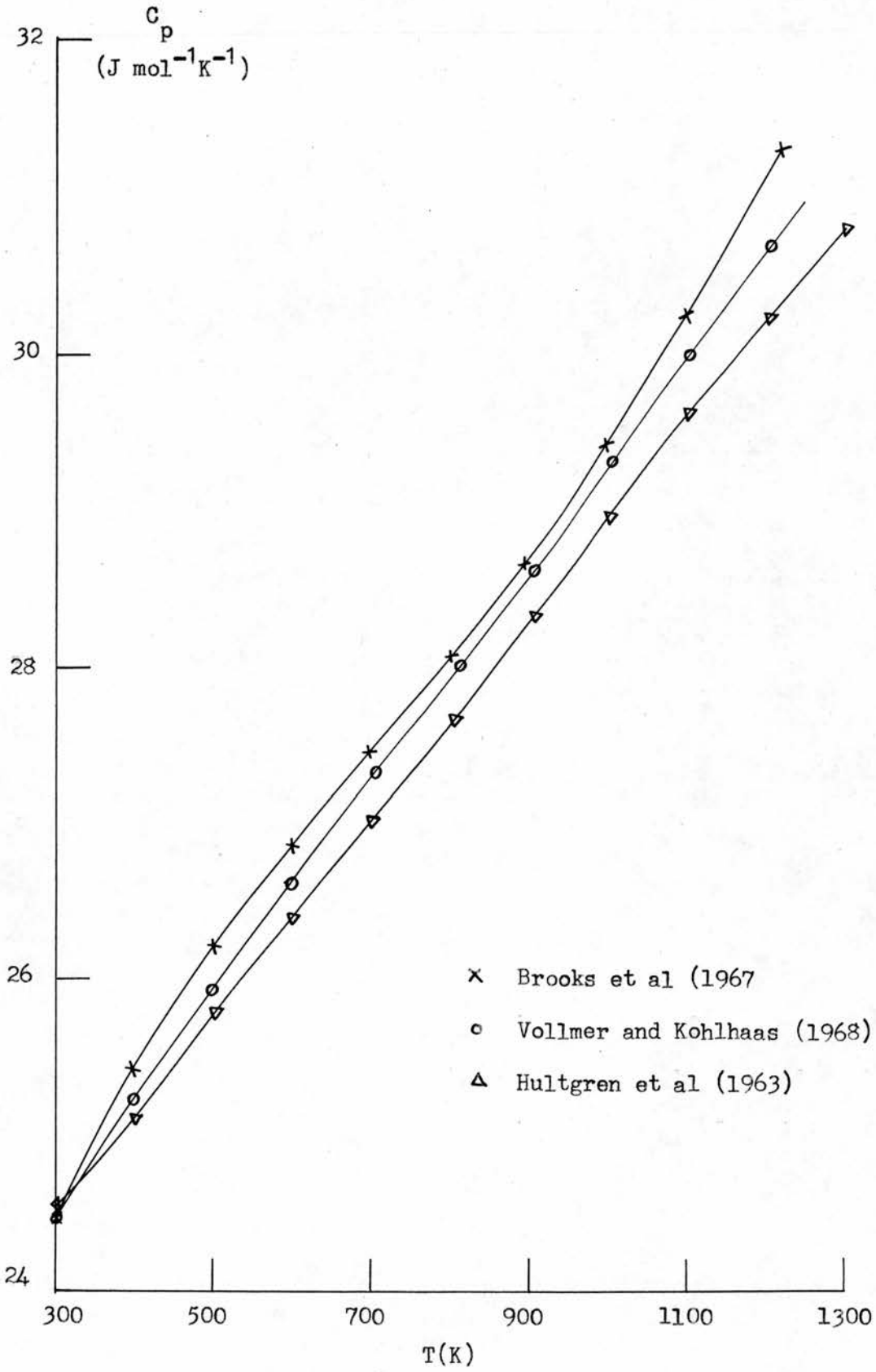


Figure 15 The experimental specific heats of copper used in the analysis.

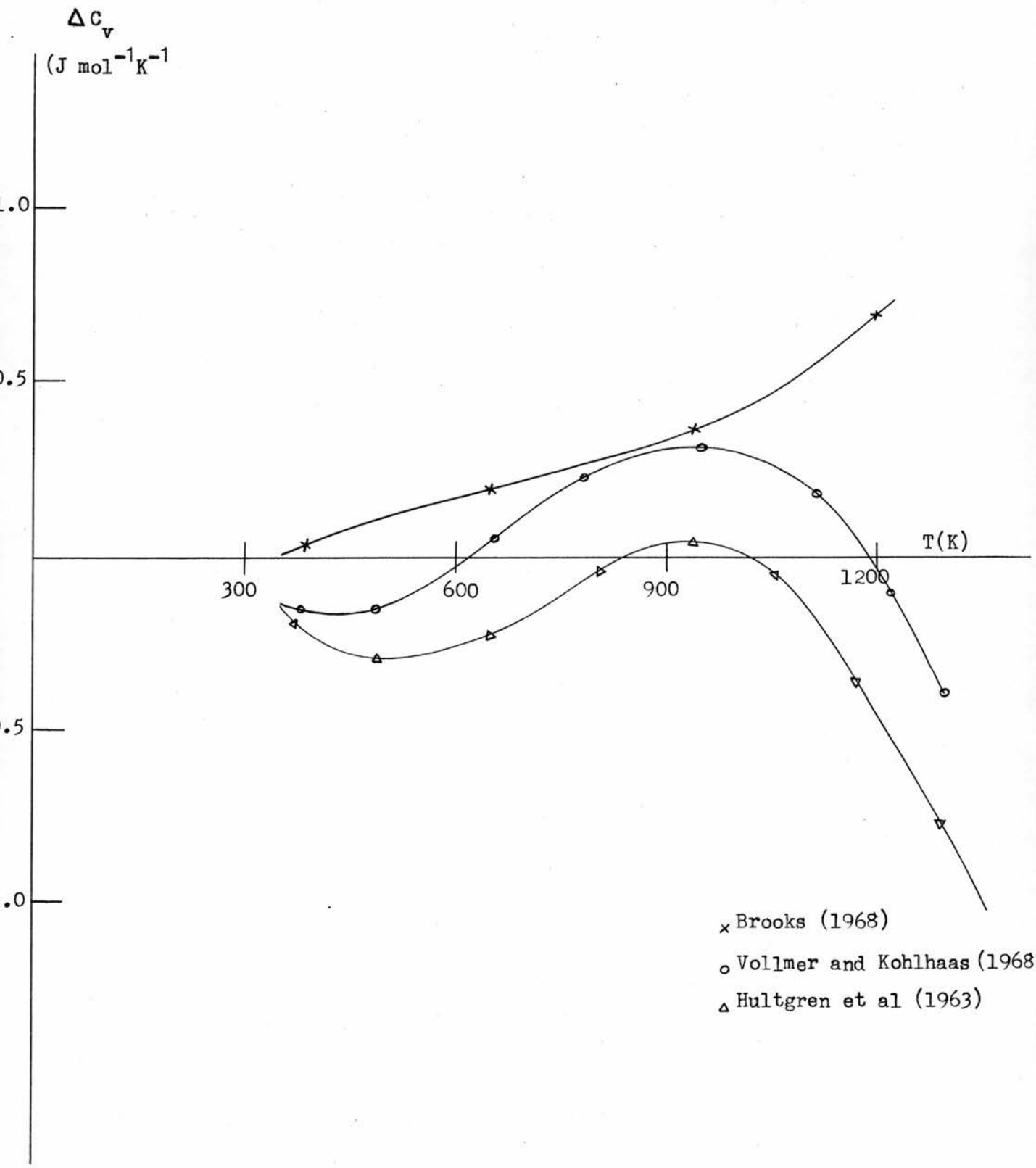


Figure 16 The excess specific heats of copper.

The C_p and ΔC_v values are shown respectively in figures 17 and 18.

Gold

C_p (a) Vollmer and Kohlhaas (1968), $\pm$ 2%

(b) Cordoba and Brooks (1971b) $\pm$ 1%

(c) Hultgren et al (1963), $\pm$ 1%

α Simmons and Balluffi (1962), $\pm$ 1%

K_a Chang and Himmel (1966), $\pm$ 2%

$W = (0.94 \pm 0.10)$eV (Simmons and Balluffi, 1962b)

$\Delta S/K = (1.0 \pm 0.5)$ (Simmons and Balluffi, 1962b)

$\gamma_x = (0.749 \pm 0.013) \times 10^{-3}$ J mol^{-1}K^{-1} (Gschneidner, 1964)

$\Theta = (165 \pm 1)$ K (Gschneidner, 1964)

Error in ΔC_v (a) 0.47 at 300K to 0.7 J mol^{-1}K^{-1} at melting point

(b) 0.24 at 300K to 0.4 J mol^{-1}K^{-1} at melting point

(c) 0.24 at 300K to 0.4 J mol^{-1}K^{-1} at melting point

Sets (a) and (b) differ significantly, by as much as 6% at the melting point, while much closer agreement exists between (a) and (c), particularly at high temperatures (see figure 19). No relation between ΔC_v and T could be given for set (b) while for set (a) and set (c) the approximate linear relation would be

$$\Delta C_v = -(1.4 \pm 0.6)\, T \times 10^{-3} \text{ J mol}^{-1}\text{K}^{-1}$$

The three sets of ΔC_v curves are shown in figure 20

8. Summary

A study of the excess specific heat calculations reveal that consistent results were only obtained for lead where the ΔC_v values

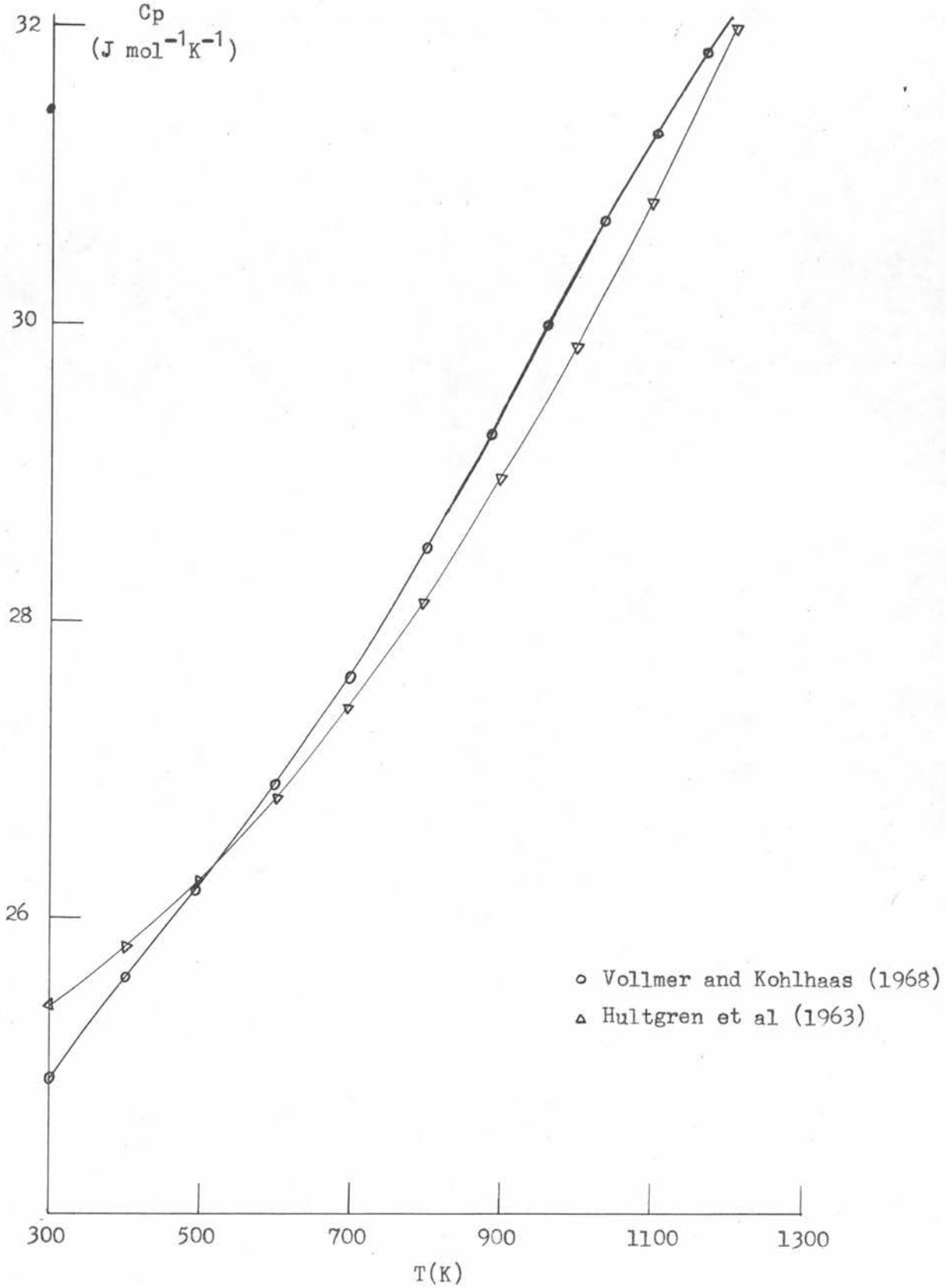


Figure 17 The experimental specific heats of silver used in the analysis.

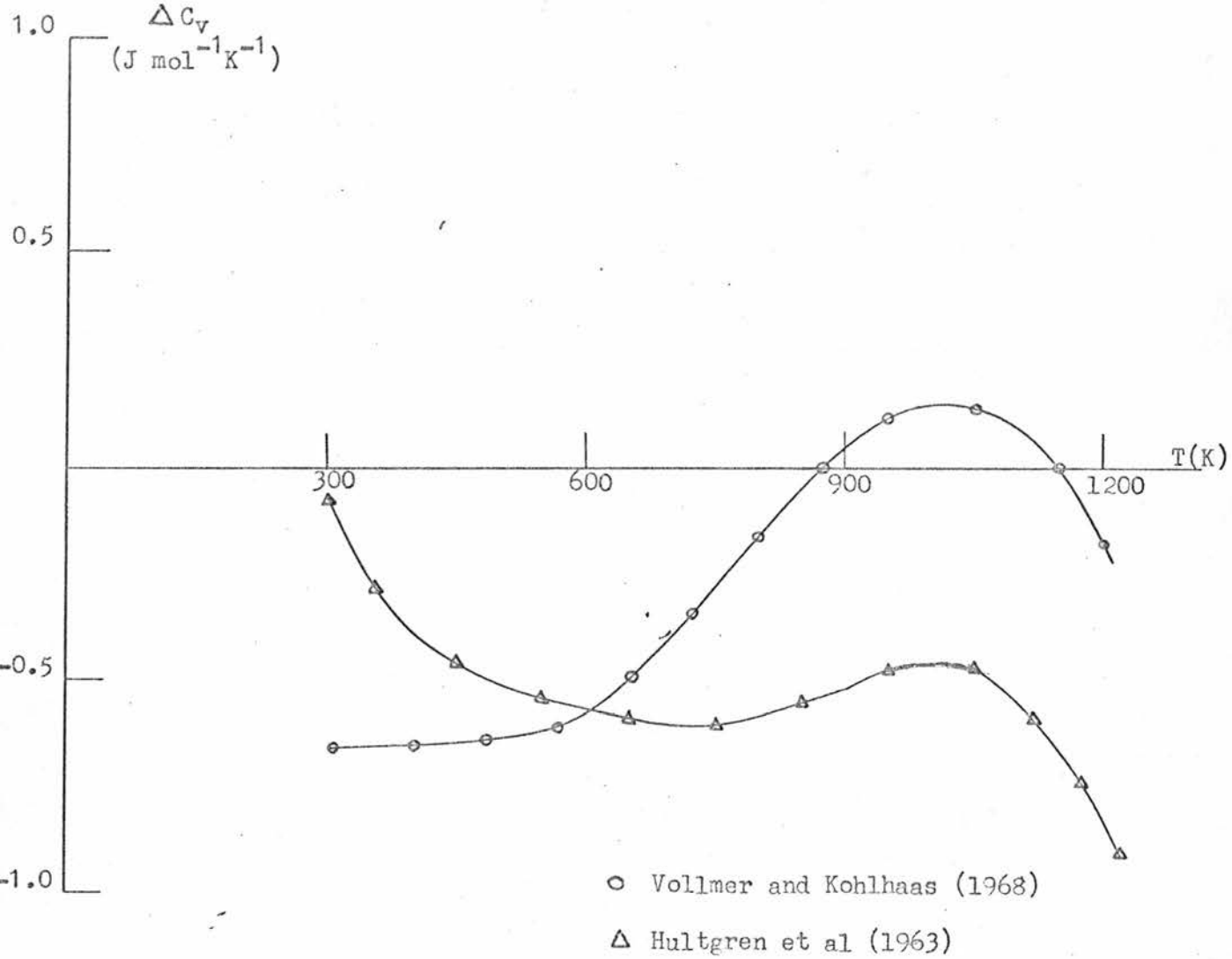


Figure 18 The excess specific heats for silver.

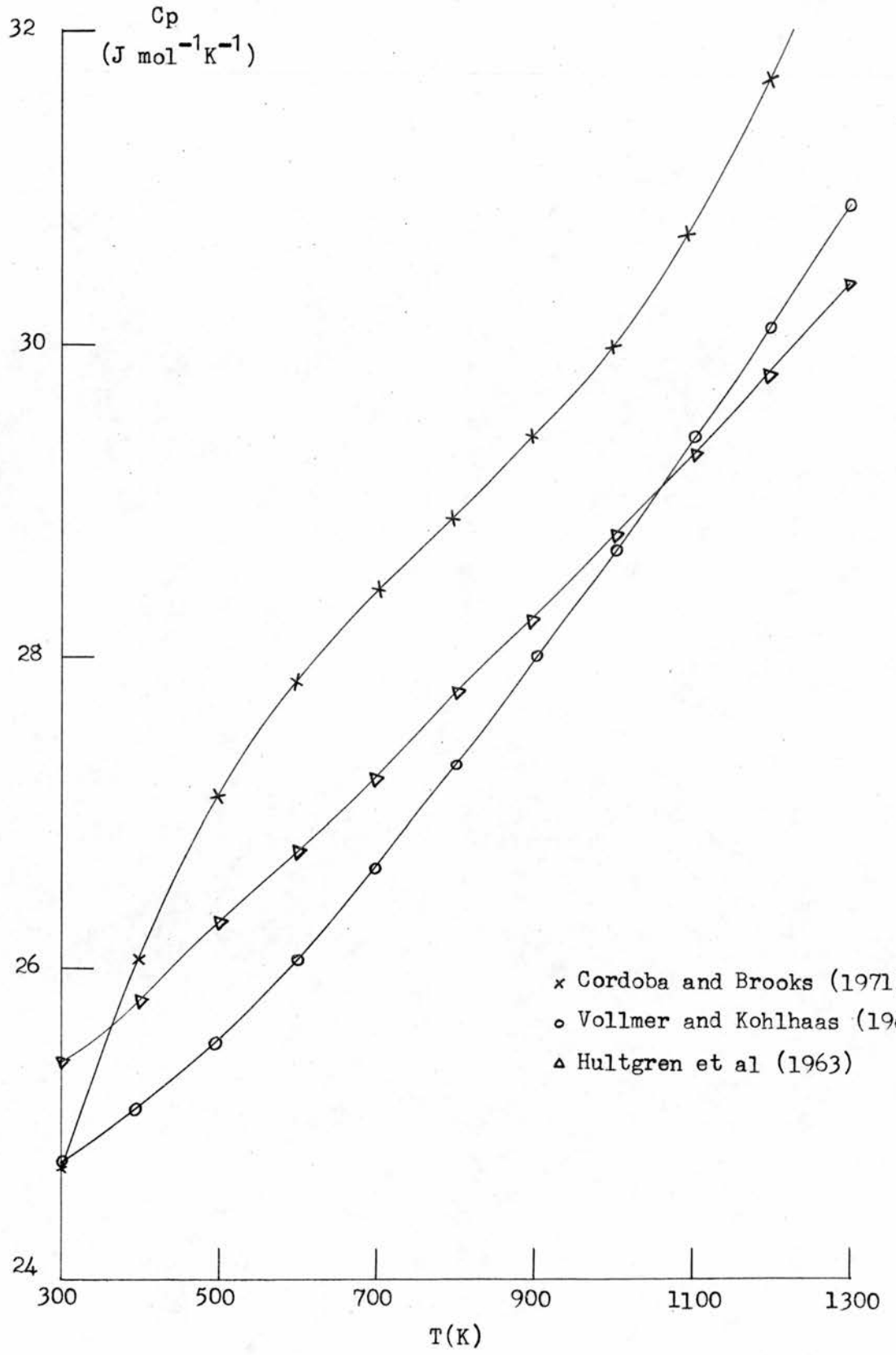


Figure 19 The experimental specific heats of gold used in the analysis.

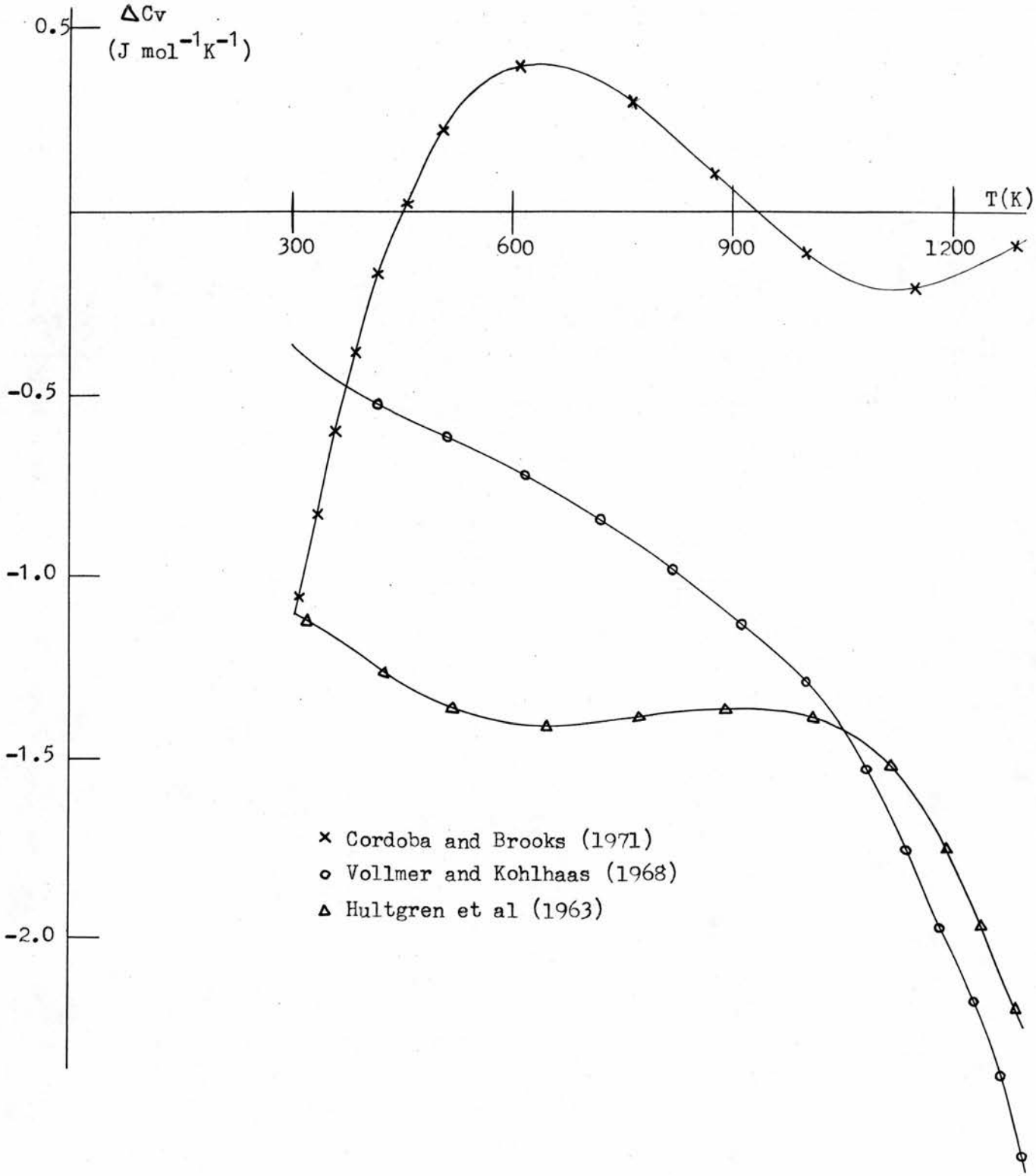


Figure 20 The excess specific heats of gold.

were always negative and varied approximately linearly with temperature (see figure 11). This consistency can be attributed to the close agreement between existing published C_p values which varied by no more than 1½% at melting point (see figure 10). A low Debye temperature (102K) enables the Debye specific heat to be determined accurately, independent of any errors in the Debye temperature, and this, coupled with the low number of vacancies which will be formed at the melting temperature of 600K, suggests an accurate determination of ΔC_v for lead. The one weakness in the lead analysis is common to most of the other materials; namely, the lack of information on compressibilities at high temperatures, necessitating the extrapolation of information into high temperature regions. In the case of lead, it was necessary to extrapolate the low temperature information of Waldorf and Alers (1962) from 300K to 600K, resulting in possible errors of $\pm$ 3% which would affect the dilation term.

The use of both theoretical and experimental electronic heat constants for lead produced significantly different values of ΔC_v at all temperatures but they did not affect the overall production of a negative excess specific heat.

Very different relationships for excess specific heats are produced for the other four materials, all of which reflects the lack of consistency in the published C_p values. In particular, the calorimetry work of Brooks and his co-workers, from 1967 to 1971, on copper, aluminium and gold produced C_p values which were consistently greater than those of other workers, suggesting that the design of their adiabatic calorimeter was subject to a systematic error. Naturally, these larger C_p values resulted in more positive excess

specific heat values being produced. In reporting these C_p values, Brooks and his co-workers also carried out an analysis similar to the present investigations and produced even larger excess specific heats for aluminium and gold, being 2.75 and 0.63 J $mol^{-1}K^{-1}$ respectively at melting point compared with 0.9 and -0.1 J $mol^{-1}K^{-1}$ obtained by this analysis of the same C_p data.

These differences in ΔC_v can be accounted for by the different values of thermal expansivities used. In aluminium, for example, Brooks and Bingham (1968) used the thermal expansivities of Wilson (1942), extrapolating his data from 600K to the melting point, and thus obtained a final value of 35.6×10^{-6} at melting point. The present analysis uses the results of Simmons and Balluffi (1960b), who obtained a value of $39.1 \times 10^{-6} K^{-1}$ at the same temperature and this difference alters the dilation term by 1.3 J $mol^{-1}K^{-1}$, bringing the two analyses more into line.

Inaccuracies in ΔC_v values, particularly at lower temperatures, will be increased in materials such as aluminium and copper which have high Debye temperatures, since any errors in the Debye temperature will have a significant effect on the Debye specific heats. As mentioned in the summary of lead, extrapolation of compressibility data is not entirely acceptable but Chang and Himmel (1966) suggested that the linear temperature dependence of compressibility in Ag, Au and Cu held remarkably well to temperatures within 80% of the absolute melting point. Aluminium was different from other materials in so far as compressibility data was available from Gerlich and Fisher (1968) up to melting point.

In conclusion an approximate linear relationship between ΔC_v and T has been obtained for aluminium, lead and gold with a negative

gradient. However, conflicting results are produced in aluminium and gold when C_p values of Brooks et al are employed. Considering the accuracies of the physical quantities used in the analysis, it must be concluded that no excess specific heat has been found for copper and silver.

Further progress in the experimental verification of the theory of solids using high temperature specific heat data can only be achieved by accurate and repeated measurements of C_p until consistent results are obtained by different experimenters. Since the expected excess specific heat is less than 2J $mol^{-1}K^{-1}$ for most materials, the C_p values will have to be measured to $\pm$ 0.2%. Sufficiently accurate measurements of the other physical parameters exist with the exception of measurements of the adiabatic compressibilities up to melting point to avoid errors caused by extrapolating existing data.

9. Grüneisen Constant

For a purely harmonic solid, the specific heats at constant volume and at constant pressure are equal, the elastic constants are independent of temperature and the solid has no thermal expansivity. However, for a real solid, both expansivity and specific heat are very much dependent on temperature since their values are determined by the distribution of vibrational frequencies of the atoms and it would be reasonable to expect a close relationship between these two properties. A study of this relationship over the complete temperature range shows that the two properties are approximately proportional, both being zero at OK and increasing proportionately as T^3 at lower temperatures. Above the Debye

temperature, the thermal expansivity increases up to melting point while the specific heat at constant volume levels off to the classical 3R value.

As the lattice expands the frequency distribution of the vibrations and the maximum frequency will vary with temperature. This will lead to a variation of the Debye temperature, Θ, with the specific volume, V, and Grüneisen (1926), using the thermodynamic relation for the free energy of a solid and taking the contribution of the lattice vibration to the free energy as that obtained from Debye theory, showed that the quantity

$$G = \frac{-d\ (\log \Theta)}{d\ (\log V)}$$

should be a constant, where G is known as the Grüneisen constant.

He also showed that G can be expressed as

$$G = \frac{3\alpha V}{K_I C_v} \qquad .. \quad .. \quad .. \quad .. \quad .. \quad (3.4)$$

where α = thermal expansivity

V = specific volume

K_I = isothermal compressibility

C_v = specific heat at a constant volume

or, alternatively,

$$G = \frac{3\alpha V}{K_a C_p}$$

where K_a = adiabatic compressibility

C_p = specific heat at a constant pressure

The Grüneisen constant can therefore be calculated at any temperature provided the experimental values of these four temperature dependent properties, namely α, V, K and C_v are known. The

variation of the Grüneisen constant with temperature can be illustrated by assuming, as a first approximation, that all these properties vary linearly with temperature. Equation (3.4) can then be re-written in the form

$$G = \frac{3(\alpha_o + \alpha' T)(V_o + V' T)}{(K_o + K' T)(C_{vo} + C_v' T)}$$

$$= \frac{3\alpha_o V_o}{K_o C_{vo}} \left[1 + T\left(\frac{\alpha'}{\alpha_o} + \frac{V'}{V_o} - \frac{K'}{K_o} - \frac{C_v'}{C_{vo}}\right)\right]$$

where $\frac{3\alpha_o V_o}{K_o C_{vo}}$ is a constant, G_o, representing the values of α, V, K and C_v extrapolated to OK. (This analysis will of course only be applicable above the Debye temperature since, at OK, the thermal expansivities and the specific heats will be zero and it does not represent the actual value of Grüneisen's constant at OK.)

By examining equation (3.4) and noting the variation of the experimental values of α and K it can be seen that $\frac{\alpha'}{\alpha_o}$ and $\frac{K'}{K_o}$ are large and positive but tend to cancel each other; $\frac{V'}{V_o}$ and $\frac{C_v'}{C_{vo}}$ are approximately an order of magnitude less. The temperature dependence of Grüneisen is therefore very dependent on the magnitude of the difference between $\frac{\alpha'}{\alpha_o}$ and $\frac{K'}{K_o}$, on the magnitude of $\frac{V'}{V_o}$, and on the magnitude and sign of $\frac{C_v'}{C_{vo}}$.

For lead, a linear variation of α, K, V and C_v with temperature is obeyed very closely and values of the relevant parameters were calculated to be:-

$$\alpha_o = 21.71 \times 10^{-6} K^{-1}, \alpha' = 2.36 \times 10^{-8} K^{-2}$$

$$\therefore \frac{\alpha'}{\alpha_o} = 0.109 \times 10^{-2} K^{-1}$$

$$V_o = 17.723 \text{ cm}^3, \quad V' = 0.18 \times 10^{-2} \text{ cm}^3\text{K}^{-1}$$

$$\therefore \frac{V'}{V_o} = 0.010 \times 10^{-2}\text{K}^{-1}$$

$$K_o = 0.185 \times 10^{-13} \text{ cm}^2 \text{ dyne}^{-1}, \quad K' = 0.018 \times 10^{-13} \text{ cm}^2 \text{ dyne}^{-1} \text{K}^{-1}$$

$$\therefore \frac{K'}{K_o} = 0.100 \times 10^{-2}\text{K}^{-1}$$

$$C_{vo} = 24.97 \text{ J mol}^{-1}\text{K}^{-1}, \quad C_v' = -0.33 \times 10^{-2} \text{ J mol}^{-1}\text{K}^{-2}$$

$$\therefore \frac{C_v'}{C_{vo}} = -0.013 \times 10^{-2}\text{K}^{-1}$$

$$\therefore G = G_o \left[1 + (0.109 + 0.010 - 0.100 + 0.013) \times 10^{-2}T\right]$$

$$= 2.5 \, (1 + 0.032 \times 10^{-2}T)$$

$$\therefore G = 2.50 + 0.0008T.$$

Hence, for lead, the Grüneisen parameter increases with temperature from 2.74 at 300K to 2.98 at its melting point.

The values of the Grüneisen parameter at temperatures between 300K and melting point were determined for Pb, Aℓ , Cu, Au, and Ag, using the same experimental values as those used for determining excess specific heat and therefore not assuming a linear variation of the physical quantities concerned with temperature.

Figures 21 and 22 show the variation of the Grüneisen constant with temperature using the specific heat data of Leadbetter (1968) for lead and aluminium and Vollmer and Kohlhaas (1968) for copper, gold and silver.

The Grüneisen constant increased with temperature for all materials, the increase being fairly linear for lead, aluminium, gold and copper according to the expressions

Lead $\quad G = (2.59 \pm 0.03) + (6.7 \pm 0.6) \times 10^{-4} T$

Aluminium $\quad G = (2.03 \pm 0.05) + (5.5 \pm 0.8) \times 10^{-4} T$

Gold $\quad G = (2.97 \pm 0.04) + (3.8 \pm 0.4) \times 10^{-4} T$

Copper $\quad G = (1.92 \pm 0.02) + (2.0 \pm 0.2) \times 10^{-4} T$

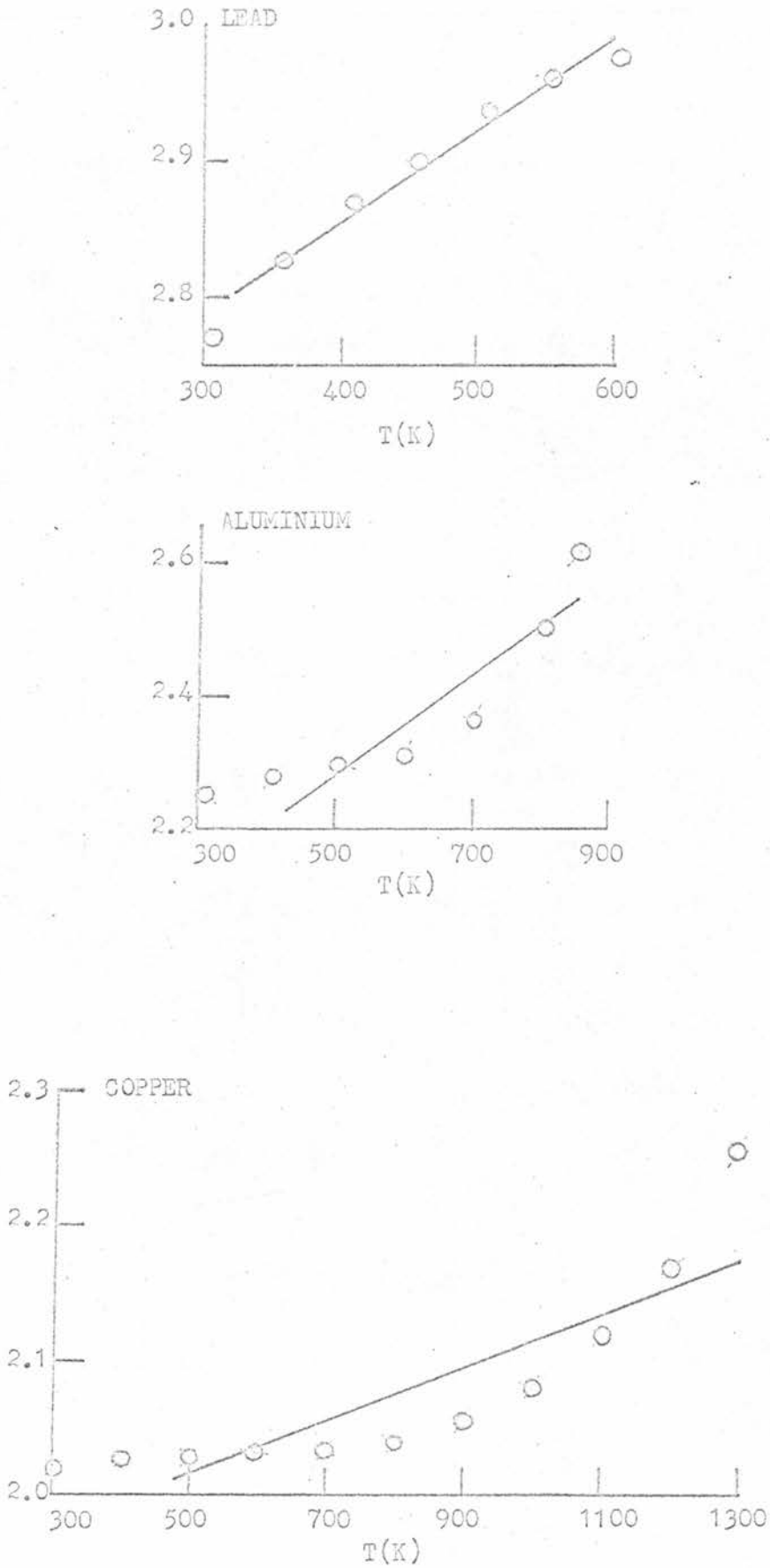
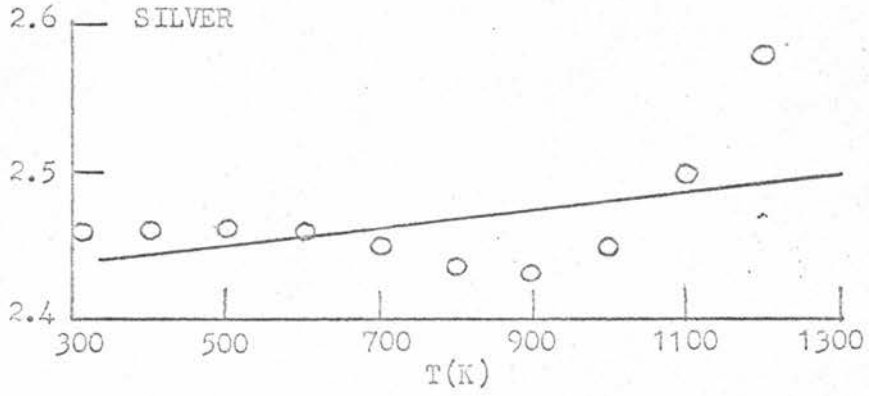


Figure 21 The variation of the Grüneisen "constant" with temperature for lead, aluminium and copper with best straight line drawn in each case.



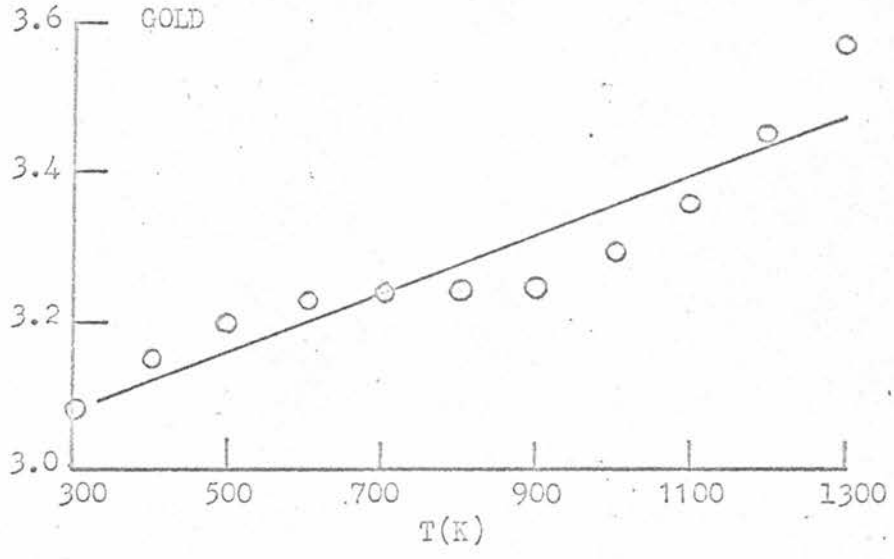


Figure 22 The variation of the Grüneisen "constant" with temperature for silver and gold, with the best straight line drawn in each case.

For copper, the Grüneisen constant is fairly constant from room temperature up to 700K and thereafter it increases rapidly up to melting point. This increase is consistent with the sudden decrease in the excess specific heat from 0.31 J $mol^{-1}K^{-1}$ at 950K to -0.34 J $mol^{-1}K^{-1}$ at 1350K.

The Grüneisen constant for silver varies less than 1% from 2.45 over the temperature range 300K to 1000K, thereafter increasing to 2.58 at 1200K. A linear expression for G may be

$$G = (2.42 \pm 0.02) + (0.6 \pm 0.3) \times 10^{-4} T$$

Gschneidner (1964) lists a range of Grüneisen constants obtained from literature and these are listed along with the present values in the following table and it can be seen that there is a close agreement.

	Literature Values	Present Results
Lead	2.62 ± 0.27	2.78
Aluminium	2.19 ± 0.1	2.24
Copper	2.00 ± 0.08	2.02
Silver	2.36 ± 0.12	2.46
Gold	3.04 ± 0.04	3.08

Brooks and Bingham (1968) and Brooks (1968) determined the Grüneisen constant for aluminium and copper respectively and found it to fall linearly from room temperature to melting point. This contradiction of the present results can be explained by the fact that these workers did not correct their C_v values for either electronic or defect contributions. In the case of aluminium the Grüneisen constant was further underestimated by the use of Wilson's expansivity results extrapolated linearly in the higher temperature regions.

APPENDIX I

Computer output shows the values of the Debye temperature, the electronic heat constant and the energy and entropy of formation of the monovacancies. The C_p values are those obtained by three point interpolation of the experimental data and the C_v^D data are those calculated from the Debye function. The excess specific heat, ΔC_v, values are obtained from

$$\Delta C_v = C_p - C_v^D - C_x - C_E - C_D \quad .. \quad .. \quad .. \quad (3.2)$$

where C_p = specific heat at constant pressure

C_v^D = Debye specific heat

C_x = dilation term

C_E = electronic specific heat

C_D = vacancy contribution

and the Gruneisen constant, G, from

$$G = \frac{3\alpha V}{K_I C_v} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3.4)$$

where α = linear thermal expansivity

V = specific volume

K_I = isothermal compressibility

C_v = specific heat at constant volume

ANALYSIS OF SPECIFIC HEAT DATA FOR LEAD

SPECIFIC HEAT DATA OF LEADBETTER(1968)

DEBYE TEMPERATURE= 102.0 K
ELECTRONIC HEAT CONSTANT=0.001505 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.50 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
26.48	24.74	1.71	0.45	0.00	-0.42	2.713	300.0
26.90	24.79	2.10	0.52	0.00	-0.53	2.757	350.0
27.37	24.84	2.53	0.60	0.00	-0.61	2.793	400.0
27.91	24.88	2.99	0.67	0.01	-0.65	2.821	450.0
28.52	24.91	3.47	0.75	0.04	-0.67	2.840	500.0
29.23	24.93	3.98	0.82	0.10	-0.62	2.849	550.0
30.06	24.93	4.51	0.90	0.22	-0.51	2.849	600.0

ANALYSIS OF SPECIFIC HEAT DATA FOR LEAD

SPECIFIC HEAT DATA OF CORDOBA AND BROOKS (1971)

DEBYE TEMPERATURE= 102.0K
ELECTRONIC HEAT CONSTANT=0.001505 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.50 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
26.49	24.74	1.71	0.45	0.00	-0.41	2.712	300.0
26.89	24.79	2.10	0.52	0.00	-0.54	2.758	350.0
27.33	24.84	2.53	0.60	0.00	-0.65	2.797	400.0
27.72	24.88	2.98	0.67	0.01	-0.84	2.841	450.0
28.25	24.91	3.47	0.75	0.04	-0.93	2.868	500.0
28.94	24.93	3.97	0.82	0.10	-0.90	2.879	550.0
29.80	24.93	4.51	0.90	0.22	-0.77	2.876	600.0

ANALYSIS OF SPECIFIC HEAT DATA FOR LEAD

SPECIFIC HEAT DATA OF HULTGREN ET AL (1963)

DEBYE TEMPERATURE= 102.0 K
ELECTRONIC HEAT CONSTANT=0.001505 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.50 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
26.43	24.74	1.71	0.45	0.00	-0.46	2.717	300.0
26.92	24.79	2.10	0.52	0.00	-0.50	2.754	350.0
27.42	24.84	2.53	0.60	0.00	-0.56	2.788	400.0
27.90	24.88	2.99	0.67	0.01	-0.66	2.822	450.0
28.38	24.91	3.47	0.75	0.04	-0.81	2.854	500.0
28.85	24.93	3.97	0.82	0.10	-0.98	2.888	550.0
29.34	24.93	4.50	0.90	0.22	-1.22	2.923	600.0

ANALYSIS OF SPECIFIC HEAT DATA FOR LEAD

SPECIFIC HEAT DATA OF LEADBETTER(1968)

DEBYE TEMPERATURE= 102.0K
ELECTRONIC HEAT CONSTANT=0.003140 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.50 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_I	C_E	C_D	ΔC_v	G	T(K)
26.48	24.74	1.71	0.94	0.00	-0.91	2.769	300.0
26.90	24.79	2.10	1.09	0.00	-1.10	2.823	350.0
27.37	24.84	2.53	1.25	0.00	-1.27	2.871	400.0
27.91	24.88	2.99	1.41	0.01	-1.39	2.909	450.0
28.52	24.91	3.47	1.57	0.04	-1.49	2.939	500.0
29.23	24.93	3.98	1.72	0.10	-1.52	2.959	550.0
30.06	24.93	4.51	1.88	0.22	-1.50	2.969	600.0

ANALYSIS OF SPECIFIC HEAT DATA FOR LEAD

SPECIFIC HEAT DATA OF CORDOBA AND BROOKS (1971)

DEBYE TEMPERATURE= 102.0K
ELECTRONIC HEAT CONSTANT=0.003140J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.50eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
26.49	24.74	1.71	0.94	0.00	-0.90	2.767	300.0
26.89	24.79	2.10	1.09	0.00	-1.11	2.824	350.0
27.33	24.84	2.53	1.25	0.00	-1.30	2.875	400.0
27.72	24.88	2.98	1.41	0.01	-1.58	2.930	450.0
28.25	24.91	3.47	1.57	0.04	-1.75	2.969	500.0
28.94	24.93	3.97	1.72	0.10	-1.80	2.991	550.0
29.80	24.93	4.51	1.88	0.22	-1.75	2.997	600.0

ANALYSIS OF SPECIFIC HEAT DATA FOR LEAD

SPECIFIC HEAT DATA OF HULTGREN ET AL (1963)

DEBYE TEMPERATURE= 102.0 K
ELECTRONIC HEAT CONSTANT=0.003140 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.50 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
26.43	24.74	1.71	0.94	0.00	-0.95	2.773	300.0
26.92	24.79	2.10	1.09	0.00	-1.07	2.820	350.0
27.42	24.84	2.53	1.25	0.00	-1.22	2.865	400.0
27.90	24.88	2.99	1.41	0.01	-1.40	2.910	450.0
28.38	24.91	3.47	1.57	0.04	-1.62	2.955	500.0
28.85	24.93	3.97	1.72	0.10	-1.88	3.000	550.0
29.34	24.93	4.50	1.88	0.22	-2.20	3.049	600.0

ANALYSIS OF SPECIFIC HEAT DATA FOR ALUMINIUM

SPECIFIC HEAT DATA OF LEADBETTER (1968)

DEBYE TEMPERATURE=423.0K
ELECTRONIC HEAT CONSTANT=0.000911 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.75 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 2.20

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.10	22.62	1.07	0.27	0.00	0.13	2.232	300.0
24.76	23.23	1.32	0.31	0.00	-0.10	2.242	350.0
25.39	23.62	1.59	0.36	0.00	-0.19	2.251	400.0
26.00	23.00	1.88	0.40	0.00	-0.20	2.261	450.0
26.60	24.10	2.20	0.45	0.00	-0.15	2.268	500.0
27.16	24.25	2.52	0.50	0.00	-0.11	2.276	550.0
27.71	24.36	2.87	0.54	0.00	-0.08	2.284	600.0
28.22	24.45	3.27	0.59	0.02	-0.11	2.307	650.0
28.72	24.52	3.69	0.63	0.04	-0.18	2.329	700.0
29.18	24.58	4.23	0.68	0.09	-0.41	2.390	750.0
29.63	24.64	4.81	0.72	0.16	-0.72	2.451	800.0
30.04	24.66	5.62	0.77	0.28	-1.30	2.575	850.0

ANALYSIS OF SPECIFIC HEAT DATA FOR ALUMINIUM

SPECIFIC HEAT DATA OF BROOKS AND BINGHAM(1968)

DEBYE TEMPERATURE= 423.0K
ELECTRONIC HEAT CONSTANT=0.000911J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.75eV
ENTROPY OF FORMATION OF MONOVACANCIES= 2.20

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.32	22.62	1.07	0.27	0.00	0.35	2.212	300.0
25.04	23.23	1.32	0.31	0.00	0.16	2.217	350.0
25.78	23.62	1.59	0.36	0.00	0.19	2.217	400.0
26.41	23.90	1.89	0.40	0.00	0.20	2.225	450.0
26.98	24.10	2.20	0.45	0.00	0.22	2.235	500.0
27.58	24.25	2.53	0.50	0.00	0.29	2.241	550.0
28.24	24.36	2.88	0.54	0.00	0.44	2.239	600.0
28.95	24.45	3.28	0.59	0.02	0.60	2.248	650.0
29.74	24.52	3.70	0.63	0.04	0.82	2.247	700.0
30.59	24.58	4.26	0.68	0.09	0.96	2.277	750.0
31.53	24.64	4.86	0.72	0.16	1.13	2.297	800.0
32.69	24.66	5.70	0.77	0.28	1.25	2.356	850.0

ANALYSIS OF SPECIFIC HEAT DATA FOR ALUMINIUM

SPECIFIC HEAT DATA OF HULTGREN ET AL (1963)

DEBYE TEMPERATURE= 423.0K
ELECTRONIC HEAT CONSTANT=0.000911J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.75 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 2.20

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.35	22.62	1.07	0.27	0.00	0.38	2.209	300.0
24.96	23.23	1.32	0.31	0.00	0.09	2.223	350.0
25.58	23.62	1.59	0.36	0.00	-0.00	2.235	400.0
26.20	23.90	1.88	0.40	0.00	-0.00	2.243	450.0
26.83	24.10	2.20	0.45	0.00	0.07	2.249	500.0
27.46	24.25	2.53	0.50	0.00	0.17	2.251	550.0
28.09	24.36	2.87	0.54	0.00	0.28	2.252	600.0
28.69	24.45	3.28	0.59	0.02	0.34	2.268	650.0
29.30	24.52	3.70	0.63	0.04	0.38	2.282	700.0
29.92	24.58	4.25	0.68	0.09	0.30	2.329	750.0
30.55	24.64	4.83	0.72	0.16	0.16	2.374	800.0
31.13	24.66	5.66	0.77	0.28	-0.25	2.480	850.0

ANALYSIS OF SPECIFIC HEAT DATA FOR COPPER

SPECIFIC HEAT DATA OF BROOKS ET AL 1967.

DEBYE TEMPERATURE= 342.0K
ELECTRONIC HEAT CONSTANT=0.000693 $J\ mol^{-1}\ K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 1.00eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.43	23.41	0.70	0.20	0.00	0.10	2.018	300.0
24.92	23.82	0.85	0.24	0.00	0.00	2.015	350.0
25.42	24.08	1.01	0.27	0.00	0.04	2.012	400.0
25.81	24.26	1.17	0.31	0.00	0.05	2.011	450.0
26.20	24.39	1.34	0.34	0.00	0.12	2.011	500.0
26.53	24.50	1.51	0.38	0.00	0.13	2.014	550.0
26.86	24.57	1.69	0.41	0.00	0.17	2.016	600.0
27.15	24.65	1.88	0.45	0.00	0.16	2.021	650.0
27.44	24.67	2.07	0.48	0.00	0.21	2.025	700.0
27.73	24.68	2.28	0.51	0.00	0.24	2.032	750.0
28.01	24.69	2.49	0.55	0.00	0.26	2.038	800.0
28.32	24.70	2.72	0.58	0.00	0.29	2.047	850.0
28.63	24.72	2.96	0.62	0.01	0.31	2.055	900.0
29.00	24.73	3.22	0.65	0.02	0.35	2.066	950.0
29.36	24.74	3.49	0.69	0.04	0.38	2.076	1000.0
29.81	24.75	3.79	0.72	0.07	0.46	2.087	1050.0
30.26	24.77	4.11	0.76	0.10	0.51	2.098	1100.0
30.83	24.78	4.47	0.79	0.15	0.62	2.110	1150.0
31.40	24.80	4.84	0.83	0.22	0.70	2.123	1200.0

ANALYSIS OF SPECIFIC HEAT DATA FOR COPPER

SPECIFIC HEAT DATA OF VOLLMER AND KOHLAAS (1968)

DEBYE TEMPERATURE= 342.0 K
ELECTRONIC HEAT CONSTANT=0.000693 $J\ mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 1.00 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_T	C_E	C_D	ΔC_v	G	T(K)
24.39	23.41	0.70	0.20	0.00	0.05	2.022	300.0
24.80	23.82	0.85	0.24	0.00	-0.12	2.025	350.0
25.19	24.08	1.01	0.27	0.00	-0.18	2.030	400.0
25.57	24.26	1.17	0.31	0.00	-0.18	2.031	450.0
25.94	24.39	1.34	0.34	0.00	-0.14	2.032	500.0
26.30	24.50	1.51	0.38	0.00	-0.10	2.032	550.0
26.65	24.57	1.69	0.41	0.00	-0.04	2.032	600.0
26.99	24.65	1.88	0.45	0.00	0.00	2.033	650.0
27.32	24.67	2.07	0.48	0.00	0.08	2.035	700.0
27.65	24.68	2.28	0.51	0.00	0.16	2.038	750.0
27.98	24.69	2.49	0.55	0.00	0.23	2.041	800.0
28.31	24.70	2.72	0.58	0.00	0.27	2.048	850.0
28.63	24.72	2.96	0.62	0.01	0.30	2.056	900.0
28.96	24.73	3.22	0.65	0.02	0.31	2.069	950.0
29.29	24.74	3.49	0.69	0.04	0.31	2.081	1000.0
29.63	24.75	3.79	0.72	0.07	0.27	2.100	1050.0
29.97	24.77	4.10	0.76	0.10	0.21	2.120	1100.0
30.32	24.78	4.46	0.79	0.15	0.11	2.148	1150.0
30.68	24.80	4.83	0.83	0.22	-0.00	2.176	1200.0
31.05	24.81	5.25	0.86	0.29	-0.18	2.215	1250.0
31.43	24.83	5.70	0.90	0.39	-0.39	2.257	1300.0
31.82	24.84	5.87	0.93	0.51	-0.34	2.246	1350.0

ANALYSIS OF SPECIFIC HEAT DATA FOR COPPER

SPECIFIC HEAT DATA OF HULTGREN ET AL (1963)

DEBYE TEMPERATURE= 342.0K
ELECTRONIC HEAT CONSTANT=0.000693J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 1.00 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.50	23.41	0.70	0.20	0.00	0.16	2.012	300.0
24.81	23.82	0.85	0.24	0.00	-0.11	2.024	350.0
25.12	24.08	1.01	0.27	0.00	-0.25	2.036	400.0
25.45	24.26	1.17	0.31	0.00	-0.29	2.040	450.0
25.79	24.39	1.34	0.34	0.00	-0.29	2.044	500.0
26.10	24.50	1.51	0.38	0.00	-0.29	2.047	550.0
26.42	24.57	1.69	0.41	0.00	-0.27	2.050	600.0
26.73	24.65	1.88	0.45	0.00	-0.25	2.053	650.0
27.04	24.67	2.07	0.48	0.00	-0.19	2.056	700.0
27.35	24.68	2.28	0.51	0.00	-0.13	2.061	750.0
27.67	24.69	2.49	0.55	0.00	-0.07	2.064	800.0
28.00	24.70	2.72	0.58	0.00	-0.02	2.071	850.0
28.34	24.72	2.95	0.62	0.01	0.02	2.077	900.0
28.65	24.73	3.21	0.65	0.02	0.01	2.091	950.0
28.97	24.74	3.48	0.69	0.04	-0.00	2.105	1000.0
29.28	24.75	3.78	0.72	0.07	-0.06	2.127	1050.0
29.59	24.77	4.09	0.76	0.10	-0.15	2.148	1100.0
29.90	24.78	4.45	0.79	0.15	-0.29	2.179	1150.0
30.22	24.80	4.82	0.83	0.22	-0.45	2.211	1200.0
30.53	24.81	5.23	0.86	0.29	-0.68	2.254	1250.0
30.85	24.83	5.68	0.90	0.39	-0.96	2.302	1300.0
31.15	24.84	5.85	0.93	0.51	-0.98	2.298	1350.0

ANALYSIS OF SPECIFIC HEAT DATA FOR GOLD

SPECIFIC HEAT DATA OF CORDOBA AND BROOKS (1971)

DEBYE TEMPERATURE= 165.0 K
ELECTRONIC HEAT CONSTANT=0.000749 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.94 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.00

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.66	24.61	0.92	0.22	0.00	-1.10	3.092	300.0
25.42	24.67	1.12	0.26	0.00	-0.64	3.057	350.0
26.07	24.70	1.32	0.29	0.00	-0.25	3.033	400.0
26.63	24.72	1.53	0.33	0.00	0.03	3.018	450.0
27.11	24.75	1.74	0.37	0.00	0.23	3.008	500.0
27.52	24.78	1.96	0.41	0.00	0.36	3.004	550.0
27.87	24.81	2.18	0.44	0.00	0.41	3.007	600.0
28.16	24.84	2.42	0.48	0.00	0.40	3.015	650.0
28.45	24.87	2.66	0.52	0.00	0.39	3.022	700.0
28.68	24.89	2.91	0.56	0.00	0.32	3.038	750.0
28.93	24.91	3.16	0.59	0.00	0.24	3.054	800.0
29.17	24.92	3.44	0.63	0.00	0.15	3.073	850.0
29.41	24.93	3.72	0.67	0.01	0.05	3.094	900.0
29.69	24.93	4.02	0.71	0.03	-0.01	3.118	950.0
29.97	24.94	4.35	0.74	0.04	-0.11	3.144	1000.0
30.34	24.94	4.70	0.78	0.07	-0.16	3.169	1050.0
30.72	24.94	5.07	0.82	0.11	-0.23	3.198	1100.0
31.22	24.95	5.47	0.86	0.15	-0.22	3.222	1150.0
31.73	24.95	5.91	0.89	0.21	-0.24	3.254	1200.0
32.42	24.95	6.40	0.93	0.28	-0.15	3.275	1250.0
33.11	24.94	6.92	0.97	0.36	-0.10	3.305	1300.0

ANALYSIS OF SPECIFIC HEAT DATA FOR GOLD

SPECIFIC HEAT DATA OF VOLLMER AND KOHLHAAS (1968)

DEBYE TEMPERATURE= 165.0K
ELECTRONIC HEAT CONSTANT=0.000749 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.94 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.00

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.70	24.61	0.92	0.22	0.00	-1.06	3.086	300.0
24.90	24.67	1.12	0.26	0.00	-1.16	3.121	350.0
25.10	24.70	1.31	0.29	0.00	-1.22	3.152	400.0
25.40	24.72	1.52	0.33	0.00	-1.19	3.167	450.0
25.60	24.75	1.73	0.37	0.00	-1.26	3.189	500.0
25.80	24.78	1.95	0.41	0.00	-1.35	3.208	550.0
26.00	24.81	2.17	0.44	0.00	-1.44	3.228	600.0
26.30	24.84	2.40	0.48	0.00	-1.44	3.233	650.0
26.60	24.87	2.64	0.52	0.00	-1.43	3.237	700.0
26.90	24.89	2.89	0.56	0.00	-1.44	3.245	750.0
27.30	24.91	3.14	0.59	0.00	-1.36	3.241	800.0
27.60	24.92	3.41	0.63	0.00	-1.39	3.253	850.0
28.00	24.93	3.70	0.67	0.01	-1.32	3.255	900.0
28.30	24.93	4.00	0.71	0.03	-1.38	3.276	950.0
28.70	24.94	4.32	0.74	0.04	-1.36	3.289	1000.0
29.10	24.94	4.67	0.78	0.07	-1.37	3.310	1050.0
29.40	24.94	5.03	0.82	0.11	-1.51	3.348	1100.0
29.80	24.95	5.43	0.86	0.15	-1.60	3.384	1150.0
30.10	24.95	5.85	0.89	0.21	-1.82	3.440	1200.0
30.50	24.95	6.32	0.93	0.28	-1.99	3.495	1250.0
30.80	24.94	6.82	0.97	0.36	-2.30	3.571	1300.0

ANALYSIS OF SPECIFIC HEAT DATA FOR GOLD

SPECIFIC HEAT DATA OF HULTGREN ET AL (1963)

DEBYE TEMPERATURE= 165.0K
ELECTRONIC HEAT CONSTANT=0.000749 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 0.94 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.00

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
25.41	24.61	0.93	0.22	0.00	-0.34	2.998	300.0
25.60	24.67	1.12	0.26	0.00	-0.45	3.035	350.0
25.79	24.70	1.32	0.29	0.00	-0.53	3.066	400.0
26.04	24.72	1.52	0.33	0.00	-0.55	3.088	450.0
26.29	24.75	1.74	0.37	0.00	-0.57	3.104	500.0
26.52	24.78	1.95	0.41	0.00	-0.63	3.119	550.0
26.75	24.81	2.18	0.44	0.00	-0.69	3.136	600.0
26.98	24.84	2.41	0.48	0.00	-0.76	3.149	650.0
27.21	24.87	2.64	0.52	0.00	-0.83	3.163	700.0
27.50	24.89	2.89	0.56	0.00	-0.85	3.173	750.0
27.79	24.91	3.15	0.59	0.00	-0.88	3.182	800.0
28.00	24.92	3.42	0.63	0.00	-1.00	3.206	850.0
28.21	24.93	3.70	0.67	0.01	-1.12	3.230	900.0
28.50	24.93	4.00	0.71	0.03	-1.18	3.252	950.0
28.80	24.94	4.32	0.74	0.04	-1.26	3.277	1000.0
29.05	24.94	4.66	0.78	0.07	-1.42	3.316	1050.0
29.30	24.94	5.03	0.82	0.11	-1.61	3.360	1100.0
29.55	24.95	5.42	0.86	0.15	-1.84	3.415	1150.0
29.80	24.95	5.84	0.89	0.21	-2.10	3.477	1200.0
30.09	24.95	6.30	0.93	0.28	-2.37	3.545	1250.0
30.39	24.94	6.80	0.97	0.36	-2.69	3.623	1300.0

ANALYSIS OF SPECIFIC HEAT DATA FOR SILVER

SPECIFIC HEAT DATA OF VOLLMER AND KOHLHAAS (1968)

DEBYE TEMPERATURE= 228.0 K
ELECTRONIC HEAT CONSTANT=0.000660 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 1.09 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
24.80	24.26	0.98	0.19	0.00	-0.65	2.463	300.0
25.20	24.45	1.19	0.23	0.00	-0.67	2.464	350.0
25.60	24.57	1.40	0.26	0.00	-0.64	2.464	400.0
25.90	24.66	1.61	0.29	0.00	-0.67	2.466	450.0
26.20	24.68	1.83	0.33	0.00	-0.64	2.467	500.0
26.50	24.70	2.06	0.36	0.00	-0.62	2.467	550.0
26.80	24.72	2.29	0.39	0.00	-0.61	2.466	600.0
27.20	24.73	2.54	0.42	0.00	-0.50	2.458	650.0
27.60	24.75	2.79	0.46	0.00	-0.41	2.448	700.0
28.00	24.78	3.06	0.49	0.00	-0.34	2.446	750.0
28.50	24.80	3.35	0.52	0.00	-0.18	2.435	800.0
29.00	24.82	3.67	0.56	0.00	-0.05	2.433	850.0
29.50	24.84	4.00	0.59	0.00	0.05	2.431	900.0
30.00	24.86	4.38	0.62	0.01	0.11	2.441	950.0
30.50	24.88	4.77	0.66	0.01	0.16	2.450	1000.0
31.00	24.89	5.23	0.69	0.03	0.13	2.476	1050.0
31.50	24.91	5.72	0.72	0.05	0.08	2.500	1100.0
32.00	24.92	6.29	0.75	0.07	-0.05	2.543	1150.0
32.50	24.93	6.88	0.79	0.10	-0.21	2.584	1200.0

ANALYSIS OF SPECIFIC HEAT DATA FOR SILVER

SPECIFIC HEAT DATA OF HULTGREN ET AL (1963)

DEBYE TEMPERATURE= 228.0K
ELECTRONIC HEAT CONSTANT=0.000660 J $mol^{-1}K^{-2}$
ENERGY OF FORMATION OF MONOVACANCIES= 1.09 eV
ENTROPY OF FORMATION OF MONOVACANCIES= 1.50

C_p	C_v^D	C_x	C_E	C_D	ΔC_v	G	T(K)
25.37	24.26	0.98	0.19	0.00	-0.08	2.407	300.0
25.60	24.45	1.19	0.23	0.00	-0.27	2.425	350.0
25.83	24.57	1.40	0.26	0.00	-0.41	2.442	400.0
26.08	24.66	1.61	0.29	0.00	-0.49	2.449	450.0
26.33	24.68	1.83	0.33	0.00	-0.52	2.455	500.0
26.58	24.70	2.06	0.36	0.00	-0.54	2.459	550.0
26.83	24.72	2.29	0.39	0.00	-0.58	2.463	600.0
27.12	24.73	2.53	0.42	0.00	-0.58	2.464	650.0
27.42	24.75	2.79	0.46	0.00	-0.59	2.465	700.0
27.75	24.78	3.06	0.49	0.00	-0.58	2.468	750.0
28.09	24.80	3.34	0.52	0.00	-0.58	2.471	800.0
28.50	24.82	3.66	0.56	0.00	-0.54	2.476	850.0
28.92	24.84	3.99	0.59	0.00	-0.51	2.481	900.0
29.40	24.86	4.36	0.62	0.01	-0.46	2.492	950.0
29.89	24.88	4.75	0.66	0.01	-0.43	2.502	1000.0
30.37	24.89	5.22	0.69	0.03	-0.47	2.529	1050.0
30.85	24.91	5.69	0.72	0.05	-0.53	2.555	1100.0
31.35	24.92	6.26	0.75	0.07	-0.68	2.597	1150.0
31.85	24.93	6.85	0.79	0.10	-0.83	2.639	1200.0

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